Development of recovery processes for recycling of valuable components from FPDs (In, Y, Nd) for the production of high added value NPs

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Content:

1. EXECUTIVE SUMMARY

The aim of the project RECYVAL-NANO, funded by European Commission over the past four years, has been the development of recycling processes for recovery and reuse of critical metals. More in detail, the focus of the project were the recovery of indium, yttrium and neodymium metals from Flat Panels Displays (FPD), one of the most growing waste sources. RECYVAL-NANO objectives included the validation of the recycling techniques developed through the construction, optimisation and demonstration of pilot lines for mechanical recycling of FPDs and hydrometallurgical metal recovery processes. Finally, in order to demonstrate the superior performance application of nanoparticles produced, the objectives of the project have been focused to apply these materials in final products such as indium in transparent conductors, yttrium in LEDs and neodymium in permanent magnets, completing the entire cycle of the project.

The treatment facilities of Coolrec Belgium located in Tisselt (Belgium) were made available for the project development. In order to increase the recovery and purity of the fractions of interest, significant modifications in the pre-disassembly process of the FPD-line were validated giving a FPD recycling process with a capacity of 800-900 kg/hour where glassplates containing indium were selected as target fraction for indium recovery. This fraction was treated by combination of a shredding plus a spinner system for maximizing the separation of the indium coated glass from the rest of the panel. In addition, a mixed powder resulting from a crushing process from the FPD waste was selected as target fraction for the recovery of yttrium.

After mechanical recycling, solvent extraction methodologies were developed during the project, recycling of indium was made by leaching with H2SO4 as leaching acid and DEHPA as extractant achieving purities larger than 90%. Yttrium metal could be also recovered from their stream using HCl as leaching acid and Cyanex 923 and DEHPA as extractants. In addition to these routes, combined processes including precipitation were assessed. Due to the high L/S values required to extract the entire metal content during leaching processes, an alternative route based on selective precipitation steps was proposed. This methodology developed has the advantage that is suitable to treat a complex mixture of metals following the whole steps or only a part, therefore being a versatile route to be tailored for WEEE complex wastes were significant amounts of valuable metals such as indium, yttrium but also gold or silver are present.

The final major activity carried out during the project was the assessment and development of alternative final applications of indium, yttrium and neodymium. For this purpose, nanoparticles were produced based on Flame Spray Pyrolysis technology. During the project, nanoparticles were produced starting from commercial precursors and simulated recycled ones in the case of indium. Promising results were found in terms of performance for some of these nanoparticles. ITO nanoparticles were used to produce non-sintered targets at lower pressures which were used for producing conductive films by sputtering showing promising results in terms of resistivity and transparency (~95%). Characterisation of the luminescent efficiency of the produced Y2O3:Eu+3 nanophosphor revealed that the synthesised nanometric material present a higher performance even at ten times lower concentrations than micrometric materials. Finally, a mixed oxide based on neodymium, iron and boron was produced by FSP which could be used for magnets production.

Finally, the full recycling process was assessed in economic and environmental terms. Based on these aspects, main contributions and potential impacts derived of the results of RECYVAL-NANO project are to provide a viable source of indium metal for Europe minimising dependency of other countries and increasing competitiveness of the recycling business, environmental benefits such as reduction of the use of natural resources and reducing landfill operations and finally increasing competitiveness of nanotechnology in Europe for nanomaterials manufacturing companies and research based companies providing improvements in TCOs and nanophosphors.

The partners in RECYVAL-NANO have been an interdisciplinary consortium including recycling companies like COOLREC, MOS and MEAB, chemical manufacturers like ABCR, nano-based product manufacturers like TECNAN, nanoparticle end-users in high-tech products such as EPILIGHT, PQL and EXKAL and prestigious experienced RTD entities like LUREDERRA, TUDELFT, CHALMERS and TWI.

2. PROJECT CONTEXT AND OBJECTIVES

Context

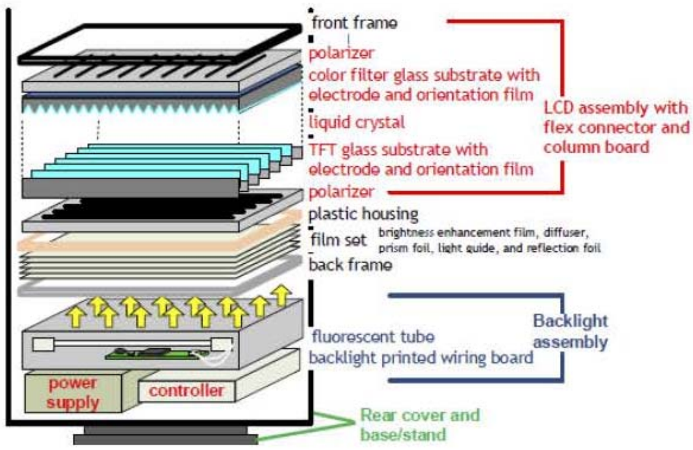
The Project Recyval-nano context has been encompassed under the concept of Reuse, Recycling and Recovery of Waste Electrical and Electronic Equipment (WEEE). Nowadays, production of modern Electrical and Electronic Equipment demand is growing every day, what involves a linked increase of the WEEE. It is estimated that 20-50 million metric tons of electronic wastes per year are currently generated worldwide. Typical end of life disposals has been landfill or incineration which cause potential emissions into the atmosphere, water contamination, and/or difficulties in biodegradation. Only a small fraction of these wastes is collected, treated and recycled correctly. Moreover, large amounts of surplus electronics are exported from developed to developing nations such as China, India and Ghana that either serve as dumping grounds or have electronic waste processing areas where uncontrolled recycling activities that involve burning cause several environmental as well as occupational health problems.

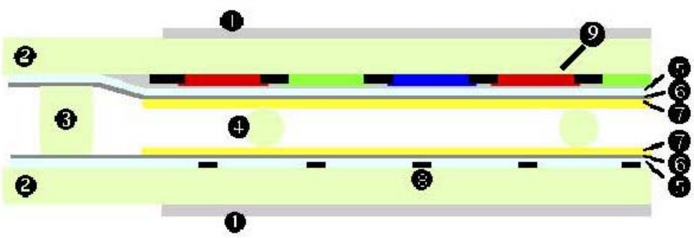
Actually, in Europe, this waste has reached an amount of 13 million tons per year. This value will increase in future decades with an expected growing rate at of least 3 to 5 % per year. Indeed, it is worth to mention that this type of waste compile a complex mixture of materials and components that can cause damages to the environment as well as health problems if they are not properly managed due to their hazardous content, since they content ferrous and non-ferrous metals, engineering plastics, precious metals, platinum group metals or rare earths metals.

On the other hand, the increase of the Electrical and Electronic Equipment demand implies the use of scarce and expensive resources that are not in Europe. Moreover, growing demand from emerging economies and the increase of national policy measures that disrupt the normal operation of global markets are making Europe highly dependent on imports for many raw materials. It is for these reasons because European Commission has established a normative about raw materials that measures in three areas to secure sustainable access from outside of Europe, improving framework conditions for extracting minerals within Europe, and promoting recycling and resource efficiency of such materials.

Within WEEE, Flat Panel Displays (FPDs) are considered one of the most promising raw materials for recycling due to represent the fastest growing e-waste since they are present in numerous electronic devices such as televisions, computers, mobile phones, etc. For example, Liquid Cristal Displays (LCDs), that is the most common FPD technology, has been increasing by 16 to 28 % every year. However, FPDs waste represents a large challenge in the industry of recycling not only for its growing rate, but also:

- To their mercury content, present in the mercury lamps employed to illuminate the image;
- Because FPDs contain a very large diversity of different materials such as metals, plastics, and glass
- And finally, due as well to the fact that it contains very different high added value metals in small fractions which are now in short supply such as Indium, Yttrium and Neodymium.





1-polarizer, 2-glass substrate, 3-seal, 4-spacer, 5-ITO, 6-passivation layer, 7-orientation film, 8-TFT, 9-color filter

Because of all these reasons, recycling processes of FPDs are in process of development and only a few large companies as Coolrec Group, Galloo and Stena are carrying out the collection and recycling of such a waste. In this context, the project has focused their expertise in the existing gap between FPDs recycling and recovery of high added value metals such as Indium, Yttrium and Neodymium. In this way, research in mechanical techniques to develop and optimize sorting technologies for FPDs has been developed in the project. This research has been carried out for analysing glass, PET and magnetic fractions in FPDs recycling processes with the aim of finding and concentrating the key metals of the project.

Secondly, after concentration of streams, development environmental friendly and cost effective solvent extraction processes was the focus of the project, not only for concentrate and recover the metals, but also with the objective of directly extract these metals in liquid solutions to be used as precursors to use them directly to produce advanced nanoparticles by Flame Spray Pyrolysis. FSP technology is the most promising technique for synthesis of high volumes at low cost of a large diversity of sophisticated inorganic oxide base nanoparticles in only one step, due to the enormously broad range of liquid precursors available. In this context, during the project the final end use of the metals could be validated through the optimization of FSP technique to produce, in one step, high added value nanoparticles such as Indium Tin oxide, Europium doped Yttria and Nd-Fe-B with lower costs due to the use of recycled metallorganic precursors in order to develop high performance technologies.

Objectives

The main objective of the project Recyval-nano is to further develop recycling processes of Flat Panel Display wastes with the aim to recover high added value metals already in short supply for direct reuse in the synthesis of high added nanoparticles to develop high technologies. In order to fulfil this ambitious and innovative objective, three major objectives were established:

1) To develop and demonstrate complete recycling processes of FPD wastes by introduction of competitive separation technologies and strategies in order to enable recovery of smaller but high valuable streams ensuring safe procedures, versatile technologies and industrial viability.

2) To develop more efficient metal extraction processes based on solvent extraction technologies in order to recover valuable metals in metallorganic precursors through modification and development of tailored solvent extraction agents based, reducing recovery steps and secondary waste stream.

3) To develop and optimise the production of advanced nanoparticles by Flame Spray Pyrolysis methods starting from recycled metallorganic precursos, promoting new highly efficient applications of the recovered materials, increasing the added value of the products from which waste was recycled and therefore ending the complete cycle.

In this way, the partial objectives to be accomplished during the different stages of the project Recyval-nano consisted on the following:

- ⇒ In WP1, as a first step, the relevant partners carried out a complete definition of i) the methodology of the collection plan of a large collection of different FPDs, ii) the most suitable sequence of sorting technologies as well as initial parameters to be tested and optimised, iii) the chemical and physical properties of the metallorganic precursors and iv) the requirements for the advanced nanoparticles of Indium, Yttrium and Neodymium.
- ⇒ The WP2 objectives were the development of mechanical separation processes for recycling FPDS and their validation at lab-scale by the fulfilment of recovery objectives of 90% in glass and PET and 80% in magnetic stream, as well as in the design and development of a pilot line able to treat 500 Kg/h of waste able to fulfil the same recovery objectives.

- ⇒ WP3 has as objective to develop the refining processes for extraction of Indium and Yttrium from glass, Indium from PET and Neodymium from magnetic powder through the development of tailored high-selective chemical agents and the development and optimization of the extraction route at lab-scales with a recovery of 95 %, to produce metallorganic precursors with a purity of 99 %. As well as to design and construct an up-scaled hydrometallurgical extraction line able to recover key metals at a rate of 500 g/hour.
- ⇒ Subsequently, the objective of the WP4 was to optimize Flame Spray Pyrolysis technique to produce advanced nanoparticles of Indium tin oxide, Europium doped Yttria and Neodymium based mixed oxide. In addition, another objective was upscaling the production to prepare 1 kg of these nanoparticles by FSP according to the industrial specifications starting from recycled metallorganic precursors.
- ⇒ Objective of the WP5 was focused in the demonstration of the pilot lines constructed by validation of the performance in trouble-free production during 16 and 8 hours, for the recycling of 500 Kg/hour of FPD waste line and the metallorganic precursor production line, respectively.
- ⇒ Finally, the objectives of WP6 were to develop and demonstrate the higher performance of i) transparent conductor coatings using ITO nanoparticles; ii) procedures in manufacture of LEDs employing high efficient nanophosphors of $Y_2O_3:Eu^{3+}$; and iii) permanent rare earths magnets based on mixed oxide nanoparticles, improving sintering density and magnetic properties in comparison with current used materials.

3. DESCRIPTION OF THE MAIN S&T RESULTS/FOREGROUND

Mechanical recycling process of FPDs for indium powder concentration

Within the RECYVAL-NANO, the first objective was focused towards regaining of critical metals from Flat Panel Displays wastes. For this purpose, Coolrec, one of the European companies leading in waste management and recycling has been working in the development of their Flat Panel Displays (FPDs) recycling process. The treatment facilities of Coolrec Belgium located in Tisselt (Belgium) were made available for the project development. This plant has a treatment capacity of 800-900 kg/hour.

Figure 1. FPDs recycling line, pre-disassembly operations

In order to increase the recovery and purity of the fractions of interest, Coolrec developed some significant modifications in the pre-disassembly process of the FPD-line giving to the selection of different extracted fractions along the FPD recycling process which were assessed during the project for metal recovery and revalorization. RECYVAL-NANO has been working over the following target fractions:

- The FPD panels or FPD plates which were manually disassembled in the preliminary stages of the recycling line. These panels contained indium in high quantities and their disassembly allows avoid metal impurities. In addition, the Coolrec recycling process including these manual disassembly fractions is still profitable with the manual operations. Additional mechanical refining was developed in this stream by partners Coolrec and MOS as it is explained in the section below.
- Dedusting processes made in FPD recycling line gives a mixed powder output stream resulting from the crushing process from a mixture of parts of FPD waste. This powder contains many metals, some of them which are valuable like yttrium, europium, indium, but also gold. Further refining of this stream during the project was assessed only by chemical extraction processes.
- Delft University of Technology has been working in the optimization of Magnetic Density Separation (MDS) for purifying the glass and fines fraction coming from the FPD recycling process. In this fraction, glass from the fluorescent lamps which contains yttrium and other rare earth metal is present. Optimization of MDS process allowed to recover a 92 % of the glass with a grade of 95 %, however, after metal analyses it was concluded that MDS refining process was not suitable for concentration of the metals of interest in the glass.

REFINING OPERATIONS FOR INDIUM EXTRACTION

Coolrec and MOS optimised a dual process in order to process the FPD panels disassembled. **By combination of a shredding plus a spinner system, it has been achieved the reduction of size while maximizing the separation of the indium coated glass from the rest of the panel**.

Figure 2. Output fractions after first shredding step

Figure 3. Output fractions after second spinning step

The metal analyses contents indicate that powders obtained after shredding and spinning were more concentrated in indium than the strips, concluding that most of the ITO coating ends in the powder output. This fraction is a valuable output as indium is present in higher quantities (> 400 ppm) and as the main metal in the stream, with iron as main impurity and others like Mo, Sn, Zn, Cu and Ni in a lower order. After this process, the fraction was suitable for extraction by chemical methods.

Versatile chemical extraction processes for valuable metals in WEEE wastes

Within the project RECYVAL-NANO, one of the main tasks in WP3 was related with the development of chemical solvent extraction processes for the recovery of valuable metals. For this reason, Chalmers University of Technology was working with different routes for the recovery of indium and yttrium present in the waste streams coming from Flat Panel Displays (FPD) wastes.

As a result of mechanical recycling work and chemical analyses, it was concluded that there are several materials of interest for the FPD recycling, resulting from different mechanical treatments of the FPDs. In particular, two fractions were of interest, one of simple composition (few metal components) and one of more complex composition (many different elements).

- This simpler material was crushed glass coming from the disassembled FPD panels (CG) which contains mainly indium.
- The second material was a mixed powder (MP) resulting from a crushing process from a mixture of parts of FPD waste. This powder contains many metals, among them yttrium.

Based on these material fractions, different processes were proposed for the recovery of indium and yttrium. Here, the main process routes are explained, including the results obtained for these processes.

SOLVENT EXTRACTION ROUTES

Two solvent extraction routes were developed, one for the CG simpler material and focused on the recovery of indium and one for the more complex material, MP for the recovery of yttrium and also indium.

The process focused on the recycling of indium from CG used 1 M H2SO4 as leaching acid and DEHPA as extractant. An indium purity >90% was achieved by two counter-current extraction and stripping stages using 0.2 M DEHPA diluted in kerosene and an addition of 15%vol TBP.

In the other process where yttrium but also indium was recovered from MP, the process was using 1 M HCl as leaching acid and Cyanex 923 and DEHPA as extractants. This process was so much more complicated than the one starting from CG due to the complexity of metals present and also the low concentration of these.

SELECTIVE LEACHING/PRECIPITATION ROUTES

The relatively low concentration of valuable metals obtained in solutions after leaching either glass (CG) or mixed waste (MP) from FPDs means large treatment facilities. The reason for this is the relatively high L/S values required to extract the entire metal content. Considering the valuable metals it would be more effective to pre-treat the leach solution and precipitate the bulk metals (in this case Al and Fe). Thus, an alternative route based on selective precipitation steps was proposed.

In order to reduce the volume size the metals are immediately precipitated after dissolution with hot 1.0 M hydrochloric acid (lower concentrations can also be used). The majority of metals are leached by the hydrochloric acid excluding some metals, for example gold. Hydrochloric acid was used since it gave the best dissolution of indium, but sulfuric acid is a possible alternative to the hydrochloric acid. The precipitation can be done in multiple ways, here sodium hydroxide was used.

The precipitate was then be re-dissolved in order to increase concentration since this way excludes the matrix of the material (glass, plastics, etc.) that was in the original sample. The re-dissolution was done in selective leaching steps to investigate if the precipitate shows equal ability to utilize selective dissolution as the original material.

An ammoniacal selective leaching step was tested in order to selevtively leach zinc simultaneously with aluminium and soldium hydroxide, however has been abandoned due to very low yeald of zinc extracted. This does, however, neglect the possibility of leaching other metals such as nickel during the ammonium-based leaching step and the ammoniacal leaching can be added if deemed appropriate depending on the composition of the waste.

Depending on the residue composition certain metals can be selectively leached from the residue using concentrated sodium hydroxide (5-10 M) or sodium hydroxide at high pressure and temperature (high pressure was not investigated but remains a possibility).

After the sodium hydroxide treatment any silver and mercury can be recovered using a thiosulfate leach solution. The original material can also be treated with a thiosulfate solution in order to recover gold. This was demonstrated to yield all the gold for the shredded glass fraction.

After the selective dissolution steps the residue can be fully re-dissolved using hydrochloric acid or sulfuric acid and a number of choices are available to recover the indium and rare earths. Sulfuric acid dissolves the indium and it prevents the re-dissolution of some metals, especially lead and strontium, which is good since they can contaminate the rare earths otherwise. Hydrochloric acid can be useful as well since a chloride based separation can be used on the solution of re-dissolved material.

The optimal choice can differ between the glass fraction (CG) and the mixed FPD fraction (MP), since the glass contains very low amounts of rare earths an acidic extractant base extraction system can be used, such as Cyanex 272 in kerosene. For the mixed FPD fraction a dual mechanism extraction system based on Cyanex 923 and Cyanex 272 was used. This allows all the indium and rare earth metals to be extracted from either a sulfuric or hydrochloric based system given a sufficiently high pH at the end of leaching. A separation can then be achieved using hydrochloric acid strip since the rare earths easily strip in such conditions leaving indium extracted. The rare earths can be recovered by selectively precipitating them with oxalic acid after strip. The indium can also be selectively extracted from the rare earths given an acidic chloride aqueous phase of sufficient chloride concentration.

It could be pointed out that this material conforms to being called WEEE in a broader sense and that the new process is suitable, in whole or parts, for WEEE recycling in general, if the WEEE in question has significant amounts of Au/Ag/Ln/Y/In/Zn.

The most important next step could be an investigation into burning the initial precipitate before re-leaching in order to create iron oxides instead of hydroxides to change the leaching behavior (reducing iron leaching levels). The dual mechanism system can also be further strengthened by showing that stripping with nitric acid (suitable pH) can separate extracted indium from iron(III). This was shown in some screening experiments but not investigated in detail.

In the following Figures, it can be seen as conclusion the flow-sheet proposed for a more complex fractions like MP and for a simpler fraction like CG.

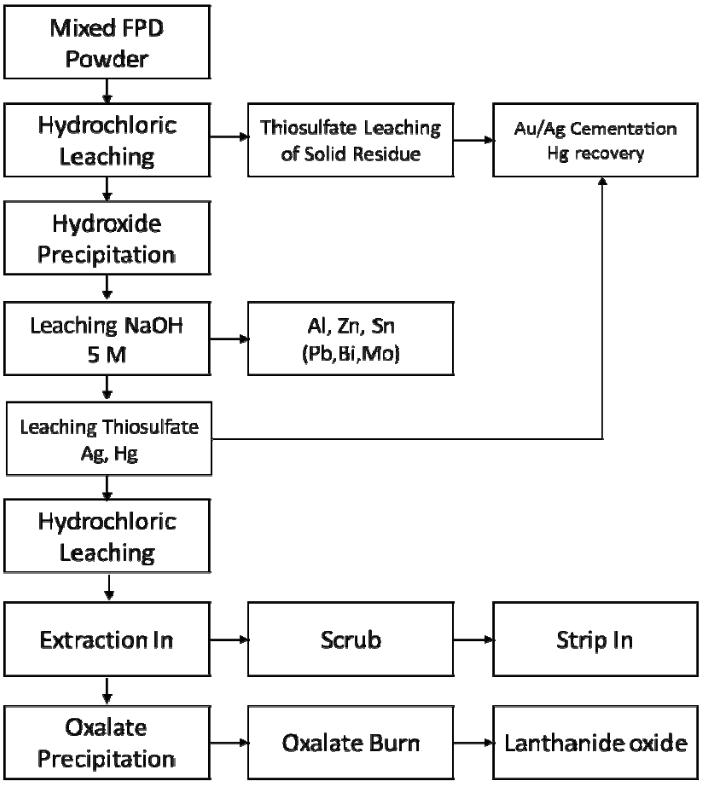


Figure 4. Treatment process flow-sheet for a fine fraction of mixed FPD powder (MP). This recovers gold, silver, rare earths and indium (simplified, there can be some purification steps excluded).

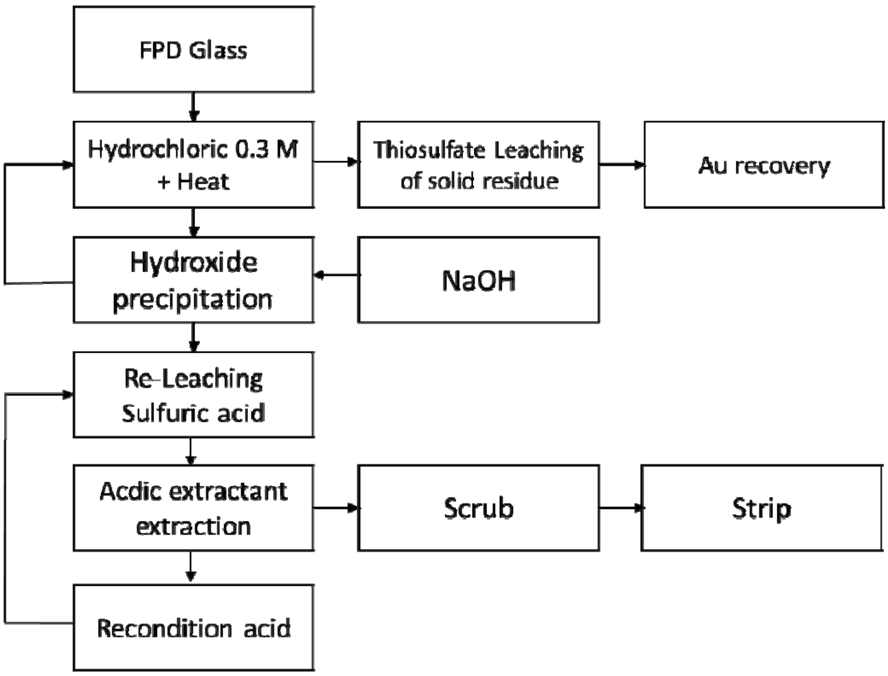


Figure 5. Treatment process flow-sheet for FPD crushed glass (CG). This recovers gold and indium.

ITO nanoparticles for Transparent Conductor Coatings

Nowadays, a wide range of high technology applications such as smartphones, tablets, solar panels or touchscreens uses thin conductive oxides based in indium-tin oxide. In this way, one of the applications developed in the project based on the importance of this metal in the market was focused in ITO.

Based on indium was one of the focus for recycling from FPDs, in addition to work in the recycling of this metal during the project, one of the targets was produce ITO nanoparticles and develop applications based on ITO but working with nanoparticles in order to assess their potential in current technologies of TCOs production and potential advantages.

In addition to the production of the nanoparticles, different approximations were followed in order to develop applications, here it is summarised the results obtained during the project. Additional information is provided in the following sections quantifying the results obtained:

- **ITO nanoparticles were synthesised by Lurederra and TECNAN in different production scales by Flame Spray Pyrolysis technology**. The results of the characterisations showed that these nanoparticles are according to requirements for final application. In addition, **these results were replicated when using simulated recycled materials**, validating the process for using secondary materials as raw materials of the process.
- Transparent coatings were produced directly from dispersion of nanoparticles and spraying reaching transparent coatings with more than 90 % of transparency.
- **ITO nanoparticles were used to produce ceramic targets** which were suitable for developing sputtering processes. Although still additional improvements are needed, the results in the project showed that nanoparticles could need lower pressures and lower thermal treatments to achieve similar densities to targets produced with conventional powders.
- Within the project, **thin conductive films have been obtained from nano-based ITO targets by Plasmaquest** partner using their proprietary HiTUS (high target utilisation sputtering) plasma deposition system, **showing promising results in terms of resistivity and transparency (~95%) when compared with coating obtained from commercial targets.** Additional improvements in ITO targets could result indeed in better results in coatings performance.

<u>CHARACTERISATION OF ITO NANOPOWDER</u>

➢ Blue powder

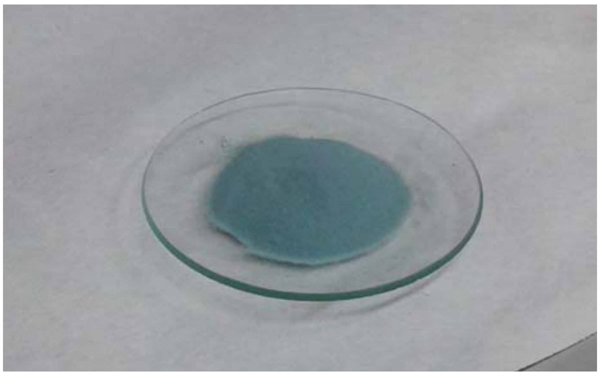


Figure 6. ITO blue powder produced from surrogate recycled materials

- Specific Surface Area of 71.98 m^2/g.

- Cubic phase.

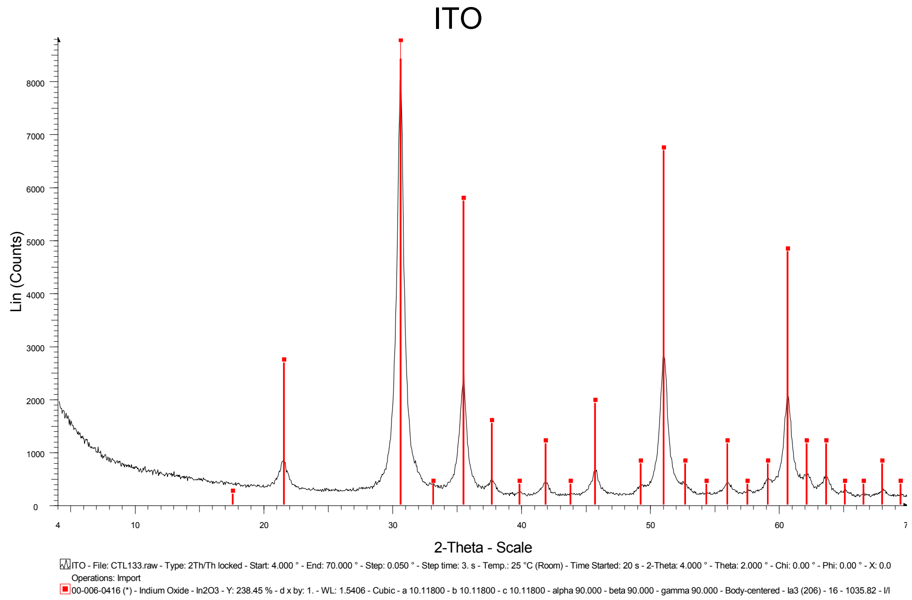


Figure 7. XRD Diffractograme of ITO

- TEM microscopy

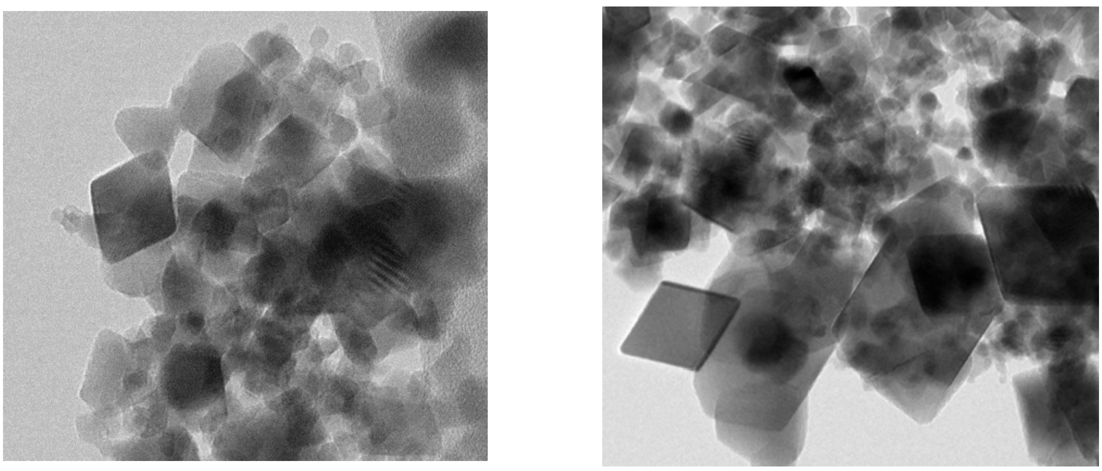


Figure 8. TEM images of ITO

- Stable dispersion of ITO nanoparticles (15% in isopropanol) for thin film spraying with average size of 29 nm.

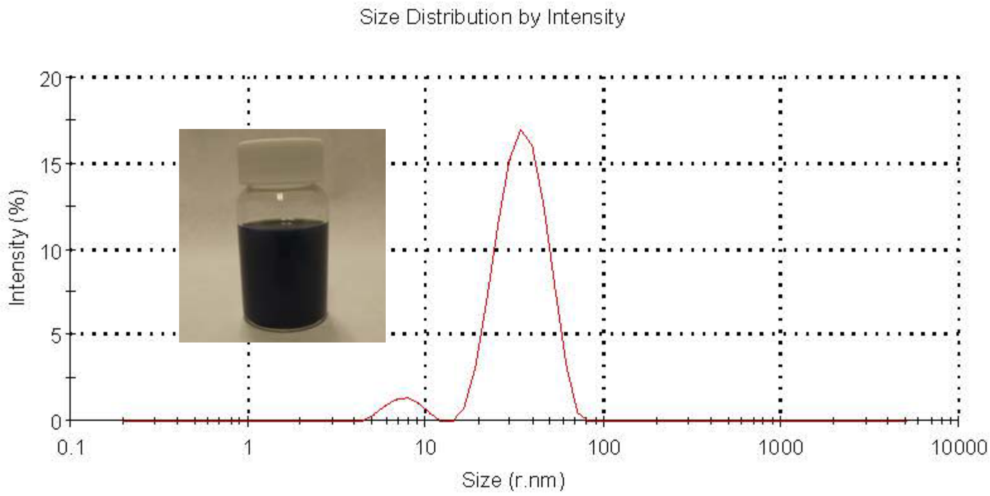


Figure 9. Size distribution of ITO nanoparticles dispersion

PRODUCTION OF ITO TARGETS

TCOs films can be obtained through different technologies; however, the technology most commonly used with this end is sputtering. To use this technique, ceramic targets have to be produced through a process based in powder compression and sintering.

Within RECYVAL-NANO it was employed ITO nanoparticles to prepare targets because, as it is well known, the surface of nanoparticles is highly reactive due to the surface area to volume ratio. This is due to the reason that most of the atoms that composes the nanoparticle are on the surface, which makes them more reactive. As a clear consequence of this, the sintering temperatures of these particles could be lower than the conventional ones and can be sintered over shorter time scales, reducing at the same time both ITO target manufacturing process and energy consumption.

ITO targets were produced during the project by means of cold pressing using a simple hydraulic press. The results indicated that densities of ITO green compacts targets of 4.75 g/cm3 were achieved with pressures of only 390 kg/cm2 where used values of pressure for compaction are in the range of 1000 to 3000 kg/cm2. Sintering of targets in the project under air atmospheres and below 1400 ºC achieved values of densities of 6.40 g/cm3 (89 % of the target).

Figure 10. Images of ITO target preparation

PRODUCTION OF ITO THIN FILMS WITH ITO NANO-BASED TARGETS

Sputtering of the ITO targets for the production of thin film coatings was developed in RECYVAL-NANO by the partner Plasmaquest using their proprietary HiTUS (high target utilisation sputtering) plasma deposition system. In this system, the plasma is generated independently of the target, this affords the benefit of being able to separately control the plasma density (ion current) and the target bias (Ar ion impact energy). Therefore, a low target bias can be applied for sputtering, which is beneficial in minimising damage to delicate targets.

Within the project, optimisation of the deposition process was made in order to be able to produce coatings from commercial sintered ITO targets and nano-based non-sintered targets produced. Although the non-sintered targets showed a slow deposition rate in comparison with commercial sintered targets, the values of resistivity obtained were only slightly higher than commercial ones. **The coatings produced could be classed as transparent conductive oxides, showing promising results in terms of resistivity and transparency (~95%) when compared with coating obtained from commercial targets.**

Target	Resistivity (Ω.cm)
Non-sintered target	$7x10^{-4}$
Commercial target	$4.5x10^{-4}$

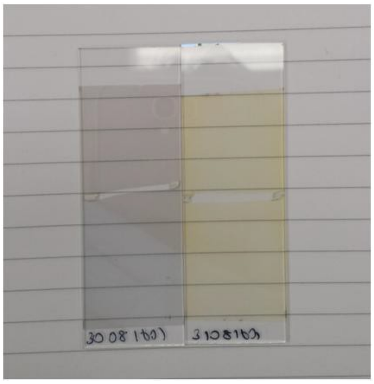


Figure 11. ITO coatings on glass from the non-sintered target (left) and a commercial target (right).

In view of the results obtained during the project, some potential aspects could be further investigated, on the one hand, if exist the possibility of suppress the sintering step or minimise the temperature in ITO targets production process and obtain thin conductive oxide films with good properties and deposition rate due to the fact of employ nanoparticles. And on the other hand, to see how far in reducing the values of resistivity could be achieved when using nano-based ITO targets decreasing to a value in the low $x10^{-4}$ Ω.cm region.

Nanoparticles as more efficient nanophosphors

Phosphors materials are able to convert light of high energy in light of lower energy. This type of materials is employed in a multitude of applications. For example they are used in radar screens, glow-in-the-dark materials, cathode ray tube, display screens, sensors or lighting.

Work Package 4 and 6 of the project RECYVAL-NANO was focused in the production of nanoparticles and application in order to validate their superior performance. In this way, during the project one typology of nanophosphor material was produced, the red phosphor $Y_2O_3:Eu^{3+}$. In particular, $Y_2O_3:Eu^{+3}$ is a dominate red emitting materials in commercial application on fluorescent lighting and display, due to its good luminescent characteristics, acceptable atmospheric stability, reduced degradation under applied voltages, and lack of hazardous constituents as opposed to sulphide phosphors.

In the past decades, the study on the luminescence properties of nano-/microcrystalline phosphors have attracted extensive interest as reduction of size in phosphors can improve the luminescence efficiency. This is because of the large surface to volume ratio of the nanoparticles, which makes them very interesting due to the quantum effect, their improved and unique properties such as high luminescent efficiency and the higher doping concentration without concentration quenching.

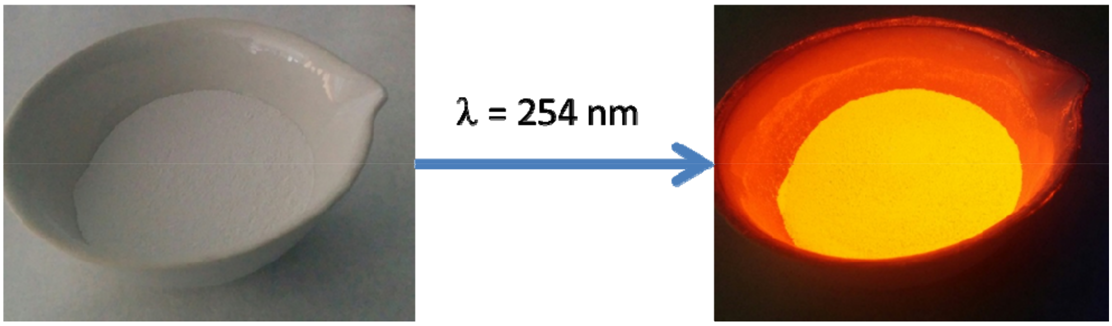
The work developed during the RECYVAL-NANO project has derived in the following achievements and conclusions for which further information is provided in the following sections:

- **Y_2O_3: Eu^{+3} nanoparticles were synthesised** by Lurederra Technological Centre by Flame Spray Pyrolysis technology. In addition, the company TECNAN worked in their scale up. **Production rates during the project were around 100 gr/hour, but the partners of the project acquired the expertise and have the technology for further upscaling**.
- Characterisation of the luminescent efficiency of the produced **Y_2O_3: Eu^{+3} nanophosphor revealed that the synthesised nanometric material present a higher conversion efficiency of UV light even at ten times lower concentrations than micrometric materials**.
- Other oxide nanophosphors can be produced by the same scalable technology (Flame Spray Pyrolysis), therefore **opening the applications and improvements derived from nanotechnology to other applications** (YAG:Ce^{+3} for LEDs, doped silicates, doped alkaline-earth metal silicates, etc.)

<u>CHARACTERISATION OF Y_2O_3/Eu^{3+} NANOPOWDER</u>

Characterization of the produced nanoparticles during the project showed the following results:

- A white powder that emits red light under UV light excitation.



- Specific Surface Area of 29.7 m^2/g.

- Cubic phase predominant.

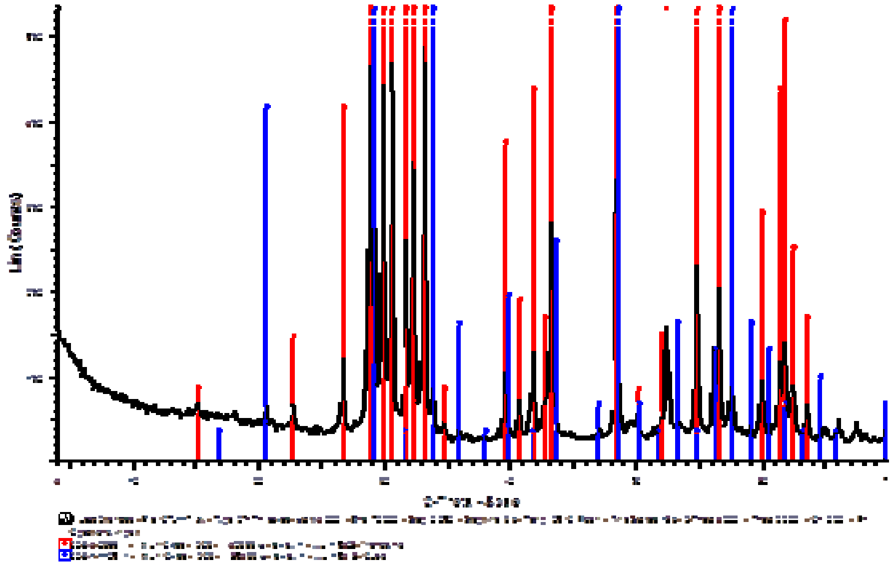


Figure 12. XRD Diffractograme of Y2O3:Eu+3

- TEM microscopy

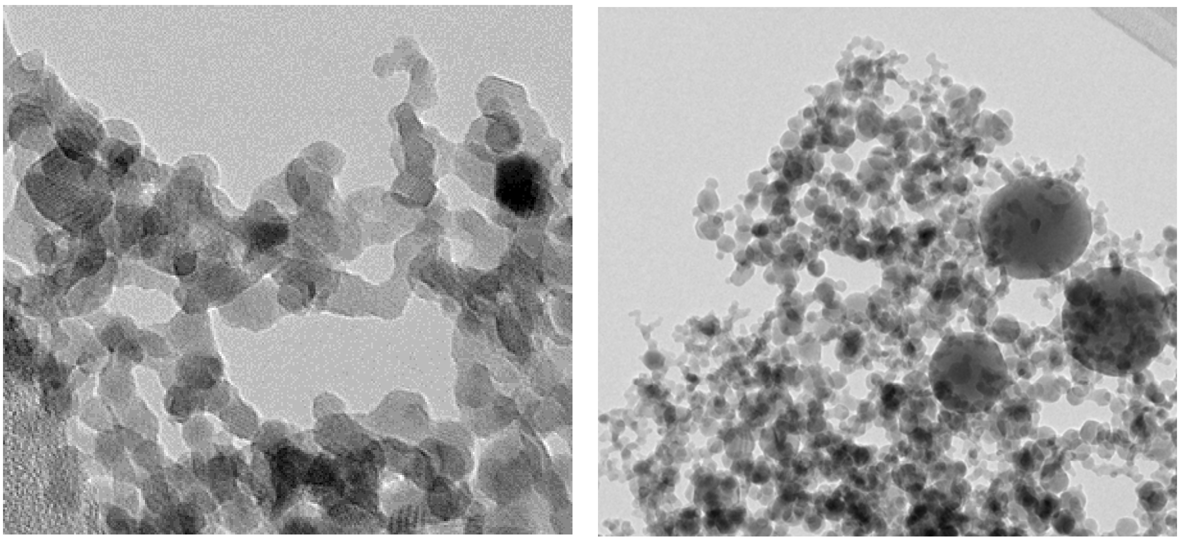


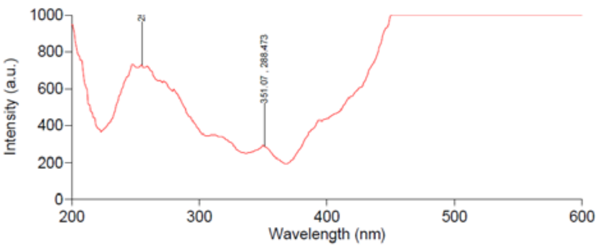
Figure 13. TEM images of Y2O3:Eu+3

LUMINISCENCE EFFICIENCY AND COMPARISON WITH MICROMETRIC PHOSPHOR

Luminescence properties of the nanoparticles were characterized in terms of excitation and emission and the results were compared with the ones obtained for Y2O3:Eu+3 microparticles.

To characterize the excitation spectra, nanoparticles and micrometric particles were irradiated in the range of 200 – 600 nm. Comparing both excitation spectra is possible to observe that the intensity of the excitation picks in the spectrum of the nanoparticles is higher event using a lower concentration of nanoparticles (0.033 mg/mL for nanoparticles vs 0.33 mg/mL for micrometric particles).

Nanometric particles **(0.03 mg/mL)** Micrometric particles **(0.33 mg/mL)**



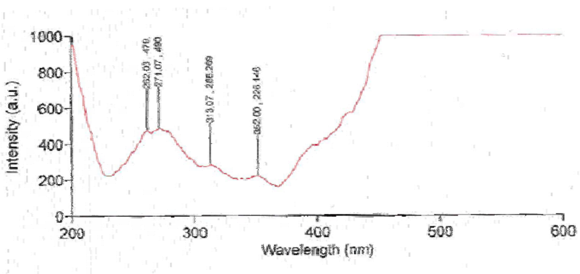


Figure 14. Excitation spectrum of Y2O3:Eu3+

By its part, characterisation of the emission spectra also revealed that **the percentage of light conversion is higher even the concentration of the nanoparticles was ten times lower than microparticles**. In the table below are included the comparative results with commercial micrometric particles.

λ_{ex} (nm)	λ_{em} (nm)	$\%_{conv}$ nanometric particles	$\%_{conv}$ micrometric particles
260	520	100	65.2.4
270	540	100	89.7.2
280	560	100	60.5.1
300	600	93.62	52.9.1
310	620	96.73	42.1.5

Figure 15. Luminiscent emission of nano and micro Y2O3:Eu3+

Nanometric particles Micrometric particles

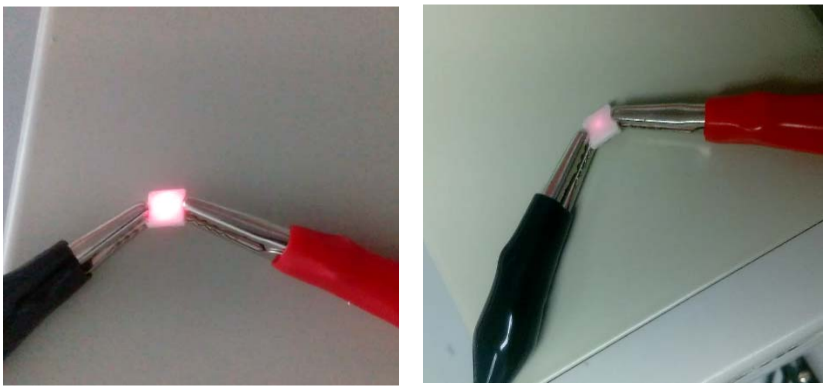


Figure . Encapsulation of Y2O3:Eu+3 phosphor in LED lighting

4. POTENTIAL IMPACT, DISSEMINATION & EXPLOITATION

Potential impact and exploitation

The most important results of the project are the assessment and validation of what recycling routes could be implemented in current Flat Panel Displays recycling lines in order to recover critical metals of great interest in Europe due to their high-tech applications. Most important results obtained gives a potential positive impact for the recovery of Indium from Flat Panel Displays as different aspects analyzed in the project like the amount of material that is available in the waste, the compositions, the continuity of the waste as well as prices volatility in the market of Indium support this idea together with the technical and economical results obtained in the recycling processes.

Around the world, 30 to 50 million tons of electronic devices are discarded every year. That volume of e-waste is expected to increase by an impressive three to five percent per year as consumers demand more and more “smart” products. One of the e-wastes which a larger growing rate are the Flat Panel Displays which although are recycled in order to recover larger fractions such as ferrous metals, non-ferrous metals, polymers, as well as mercury elimination where fluorescent lamps are present, other valuable metals present like indium are not still recovered in industrial processes.

During the project, the assessment of indium, yttrium and neodymium metals was made, however only in the case of yttrium and indium, the quantities present in the FPD were similar or indeed larger than in mine ores. As FPDs could serve as mine for the recovery of certain metals, a point which could influence this has to be highlighted which is that FPDs technology is continuously changing which makes difficult focus on recycling. For example, as concluded from the analyses made in the project, neodymium was not present as although neodymium magnets start to be present in loudspeakers, still most magnets are based on ferrites, however this could change in the future. Another example, is the change in the backlight technology used in FPDs. The first generation of FPDs based on Liquid-Crystal Display (LCD) monitors and televisions, used Cold Compact Fluorescent Lights (CCFLs), which are now the ones mostly present in the wastes streams, where the main second generation of FPD technology is based on Light-Emitting Diode (LED) and the most newer technology is based on Organic Light-Emitting Diode (OLED) monitors and televisions. Therefore, if we focus in the metals which could be present in these systems in addition to the mercury, for example the content of yttrium could vary depending the system used as backlight. In the case of indium metal, the situation is different as ITO coating over glassplates continues to be the most desired and used technology in displays.

Following the results obtained in the project, one important conclusion is that in order to the recovery of indium can be viable, disassembly actions are needed in order to separate the glassplate. The recycling process of Coolrec was adapted for the disassembly of the glassplates and a positive conclusion was that the process still could be profitable including these additional manual operations. Taking into account that Liquid Crystal Display panels or glassplates are currently a waste which ends in landfills and therefore which has to be managed and suppose a cost for the recycling process, an important impact for the recycling industries like Coolrec is that they could offer a new valuable product where Indium can be recovered out of the glass rich fraction. In addition, recovery rates will improve even better and in the vision of circular economy this part of recycling could be extended.

Although the clearest impact of the project is based on the recovery of indium from glassplates, during the project one of the chemical routes developed for extraction and refining of metals has been designed to be suitable for complex mixtures of electronic wastes where a variety of metals are present and could be recovered by selecting the required steps of the route. In this way, other increasing technologies of e-waste could be target of recycling by means of the processes developed in the project. For example, smartphones, tablets and other popular electronic products contain precious materials, including gold, copper, palladium, silver, platinum, cobalt, and more. The developments of the project open the typologies of e-wastes to be treated and therefore the potential economic incomes. Based on bibliography, estimated potential revenues from recycled e-waste are expected to rise by the year 2020 to more than 3.5 billion Euros.

Focusing on indium recovery, economic estimations shows a potential positive impact for the recycling processes developed. Although some higher scale demonstration should be made mainly in the chemical extraction processes developed, the economic estimations made at industrial scales showed that there is potential for the exploitation of the hydrometallurgical processes developed for profitable indium extraction. These analyses were made taking into account the large variability of indium prices. The range of prices in the past were between 436 €/kg to 756 €/kg. However, prices in July 2015 fallen up to 285-356 euro/kg. Just considering the lowest prices of nowadays, the processes could be profitable. Another aspect which was preliminary taking into account was the format and the purity of indium stream which by sure will affect the price that the refiners could pay for it.

However, it is worth to mention that if indium price could still go down, these could limit the profitability of the indium recovery. Also, it is important to highlight that indium price cannot decrease under $100/kg. As for production costs, analysis made in bibliography indicates that producers require a minimum indium price of $100/kg to produce indium. Below this price, even the highest-grade deposits cannot economically recover indium.

The potential impact of the processes developed for yttrium in this case are very limited as owing to abundant supply and shrinking demand in some markets, prices for yttrium metal and oxide decreased significantly and the tendency looks to be stable. Taking into account the volatility of the metal prices in the market, once again the versatile process developed for the extraction of a variety of metals in a complex mixture have a great potential impact as the line could be tailored to the extraction of the profitable metals based on the market demand in each case.

Finally the results of the project have bring also potential impacts due to the innovative applications developed with indium and yttrium metals based on ITO nanoparticles and Y2O3:Eu+3 nanoparticles. Therefore, new knowledge has been acquired for the development of high-tech applications. Based on the results obtained, the use of nanophosphors such as Y2O3:Eu+3 instead micro phosphors has a technical and economical positive impact. As previously explained nanophosphor showed better efficiency in the conversion of UV to red light even at lower concentrations. Taking into account that estimated prices of yttrium starting from recycled materials were in similar ranges than microphosphors, the economic benefits could be higher. Indeed, the results obtained in the phosphor composition developed in the project open the possibilities to develop other compositions for different fields of application.

The introduction of the technologies for indium recovery in the market will result in the reinforcement of the European recycling activities as well as raw materials processing from the recycled fractions and thus in the creation of new jobs. The achievement of this project will encourage post-treatment chemical companies for the new recovered fractions. The new demand will need the set-up of new facilities, promoting employment with skilled workers. In addition, the applications developed with nanomaterials in the project will result in the reinforcement of the European nanotechnology-based products industry, electronics industry based on ITO coatings and luminescent nano-phosphors. In this sense, it is worth noticing that the demand for these applications and nanotechnology based materials industry are constantly growing.

In addition, the results of the project have also promoted knowledge which can be extended to recycling of other materials, other critical metals, other wastes, PET polymers which will result in further research, therefore requiring multidisciplinary high-skilled figures such as recycling engineers, chemists, physicists, etc. promoting education and training activities in the different fields.

Impact on environment

Of course, the recycling of electronic waste products also promises to reduce environmental pollution by conserving virgin resources, which are required for the manufacturing of high-tech consumer products. In this way, the recycling technologies developed in RECYVAL-NANO has been assessed in environmental terms concluding that these processes are positive for the environment.

In fact, the recycling FPD process of Coolrec was analyzed and due to the large quantities of recyclable fractions which are extracted such as plastics, metals, etc., this process is beneficial for the environment as avoid the consumption of other resources. Increasing manual disassembly operations as in the project, increase the recyclability of additional materials, therefore being a better option in environmental impact.

Also, the refining and chemical steps were analyzed in terms of environmental impact and although these could have some negative inputs for the environments when a global vision is created of the mechanical and chemical process together for the recovery of indium or yttrium, the environmental situation still is positive. Indeed, when comparing production of metals from recycling in the project or mining, the environmental impact of the whole process is higher in the case of mining extraction processes, mainly due to there a lot of recycled materials in the global FPD recycling process.

In addition to the recycling and therefore minimizing the use of resources, another positive environmental impact of the project is that the target streams of the project just now are discarded and ends in most of the cases in landfills. According to the waste management hierarchy, landfilling is the least preferable option and should be limited to the necessary minimum in order to prevent or reduce as far as possible negative effects on the environment, in particular on surface water, groundwater, soil, air, and on human health from the landfilling of waste.

To summarise the potential impacts of the RECYVAL-NANO projects are:

- Increase European recycling business for the recovery of indium, involving higher recovery rates in current FPDs recycling companies and generating new business of metal chemical extraction
- Provide a viable source of indium metal for Europe minimising dependency of other countries and increasing competitiveness
- Increase recycling of wastes, FPD and depicted fractions reducing the consume of natural resource and reducing environmental consequence derived of landfill operations
- Increase understanding of nanomaterials for electronic field, providing improvements in TCOs and nanophosphors, therefore increasing competitiveness of nanotechnology in Europe for nanomaterials manufacturing companies and research based companies

Finally, the overall objective during and after the project is to maximize the uptake of the project results and potential impacts. For this purpose, the main results of the project have been disseminated by different measure which are explained in the following section.

Main dissemination activities

A project identity set consisting of the project logo as well as the RECYVAL-NANO website (http://www.recyval-nano.eu/) was created at the beginning of the project in 2013 and updated with data from all the partners and results obtained.

Articles has been published in the popular press and web sites in order to let know the project in economic and regional media of the region of some partners: Diario de Navarra or XesGalicia.

In addition, during the project, posters and oral presentations were made by the project partners at different conferences and workshops in Europe (Spain, Germany and Brussels).

Two workshops were held during the project execution. One in Los Arcos (Spain) in November 2015 in order to promote different recycling technologies of wastes including some related with the project. Second workshop was held in Brussels (Belgium) at the end of the project in November 2016 in order to explain the results of the project and their potential implications.

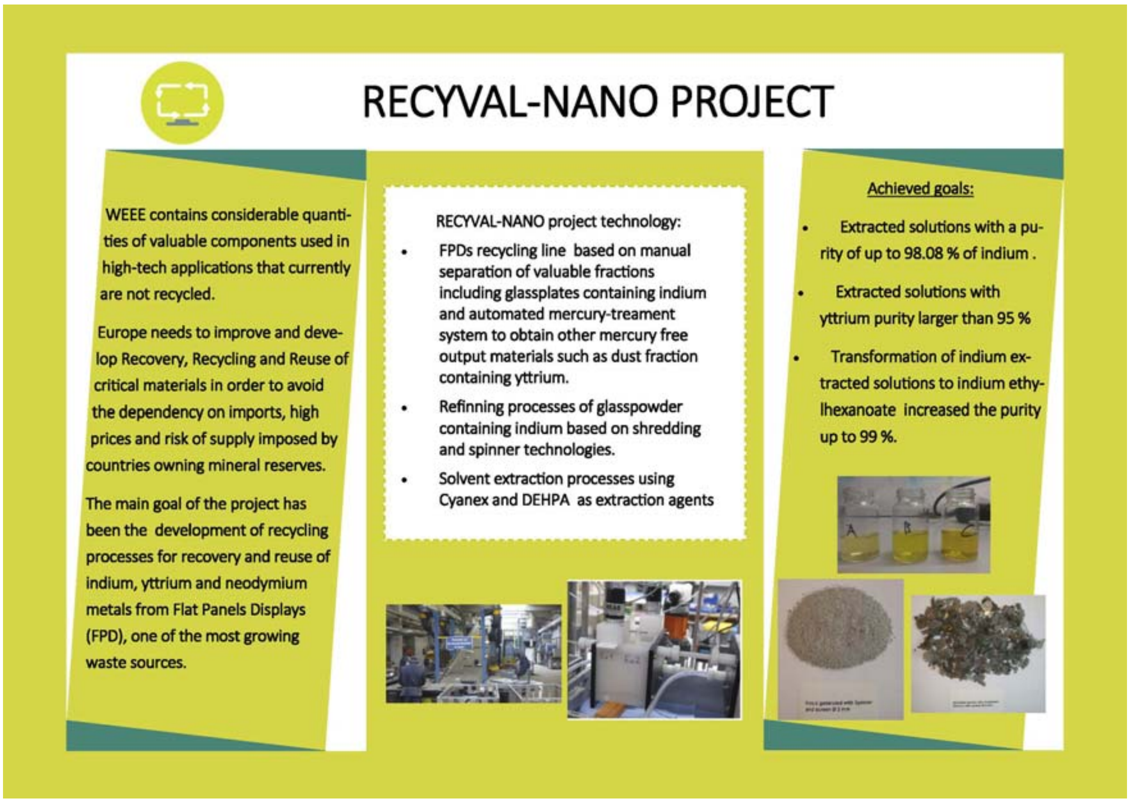
Workshops held in RECYVAL-NANO

In addition, two publications were made by Chalmers University of technology. One doctoral thesis and a publication in an international well-known journal. These are:

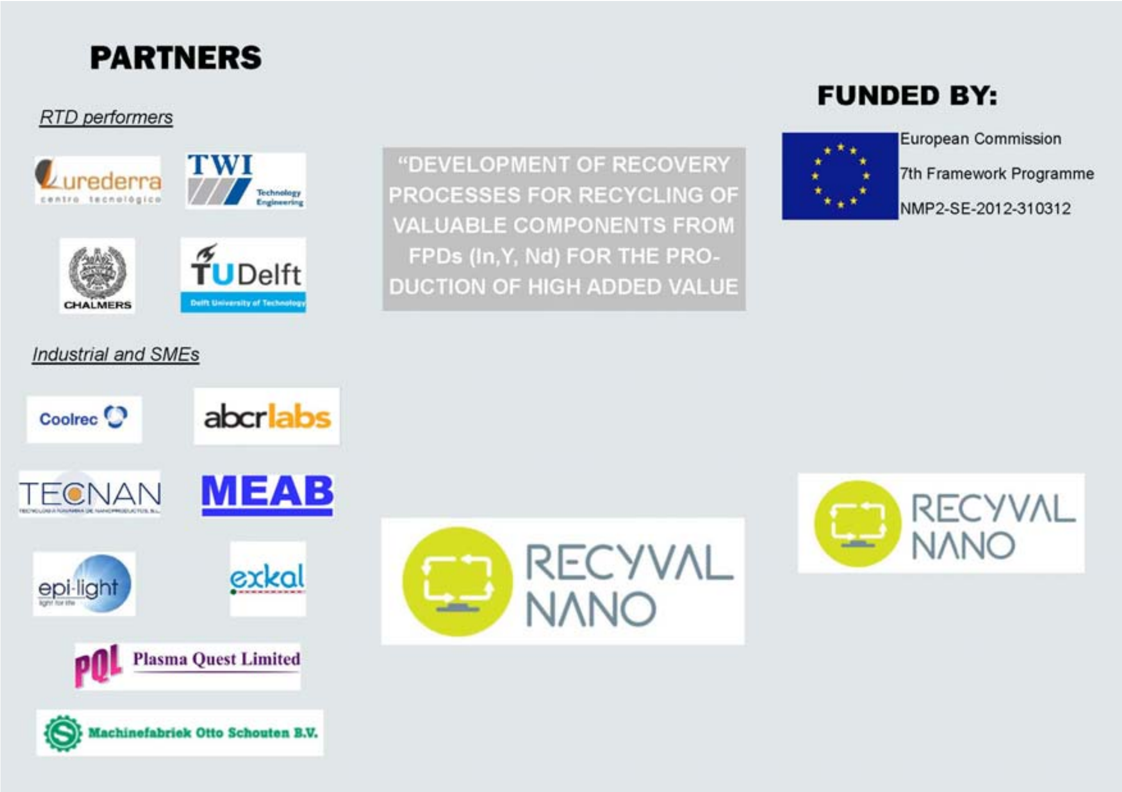
Yang, J. (2015). *Process Development for Extraction and Separation of In and Y from Discarded Flat Panel Displays. Chalmers University of Technology.* (Doctoral thesis, Chalmers University of Technology, Gothenburg, Sweden).

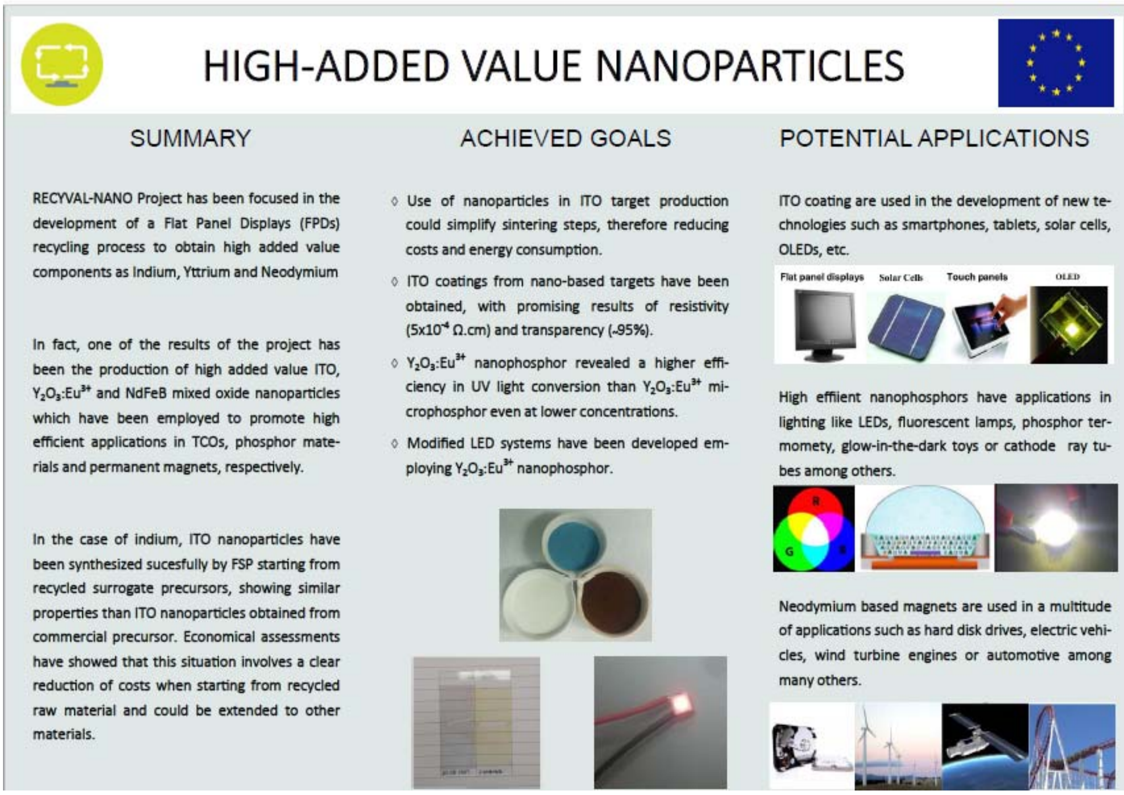
Yang, J., Retegan, T., Steenari, B., Ekberg, C. *Recovery of indium and yttrium from Flat Panel Display waste using solvent extraction*. Elsevier. 2016, 166, 117-124.

Also, divulgation of information was made through preparation of posters, flyers and brochures containing results of the recycling processes developed as well as regarding final application of nanomaterials tested.



Flyers for dissemination of RECYVAL-NANO technology





Flyers for dissemination of RECYVAL-NANO applications

Main exploitation plans

Based on the main results previously explained regarding technology, knowledge and new materials, uptake of these results through exploitation is desired. The RECYVAL consortium is interested in making available to third parties the technologies developed under the project in several ways:

a) Sale of Know How

b) Sale of equipment

c) Joint research

Third parties interested in any of the results of the project should in the first instance contact to:

*Mr. Luis Martinez de Morentin Osaba (*luis.martinez@lurederra.es*)*

*Ms. Angélica Pérez Manso (*angelica.perez@lurederra.es*)*

giving information on their areas of interest