SEVENTH FRAMEWORK
PROGRAMME

shyman

FINAL PROJECT REPORT

Project acronym:	**SHYMAN**
Project title:	Sustainable Hydrothermal Manufacturing of Nanomaterials
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Call topic:	NMP.2011.1.4-1, Large-scale green and economical synthesis of nanoparticles and nanostructures
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SHYMAN EXECUTIVE SUMMARY

In 2008 Lux Research predicted that nanoparticles would “touch” $3.1 trillion worth of products across the value chain by 2015, with the intermediates market reaching a net worth of $432 billion. Transparent conductive films alone would be worth $3.5 billion by 2020. However, it is almost impossible to find credible predictions for the market potential of the nano-enabled industry beyond 2025. Hence in 2016, it is also fair to say that nanotechnology is still a developing market with many emerging sectors. There are many different methods for producing nanomaterials to meet market demands, and dry methods (despite all the ensuing issues over safety) have been the most successful to date. As alternatives emerge, it is likely that industry will turn away from these dry products and engage with process technologies that can produce a dispersion based, higher quality and easy to formulate product. The real challenges for new alternatives are clearly around material quality, scale up, formulation and (most importantly) the cost of production.

Continuous hydrothermal synthesis is relatively new technology and would offer a true alternative to other production methods because it is a genuinely continuous process which is also chemically more benign. Continuous hydrothermal synthesis produces nanoparticulate materials by mixing superheated or supercritical water flow with an aqueous flow containing a dissolved metal salt. i.e. rather than slowly heating the entire contents of a batch vessel (batch hydrothermal synthesis), two fluids are continuously mixed together. The problems around this process were solved during research work at The University of Nottingham and the reactor configuration necessary for continuous production was demonstrated at bench (g/hr) and pilot scale (kg/day) prior to the start of the project.

Through the SHYMAN project and the interaction of the 17 partners from across Europe, the process has now been scaled to 1000 tons per year production (dry weight equivalent) which makes the plant the largest multi nanomaterial production facility in the world. Sustainability credentials and cost analysis were also assessed, to compare the process against alternative methods and against existing products in the market place. The process was shown to be highly sustainable, and cost effective with OPEX costs of below 10 euros per kilo (and less than 5 euros, in some cases). A water treatment strategy was devised and implemented that would allow the plant to operate continuously whilst formulating products, ready for sale.

Case studies were part of the project in order to validate the products in the context of real products. These products were selected to demonstrate the efficacy of the process in different areas from healthcare to printed electronics. Each area required particularly performance criteria that would test how controllable the process was in terms of product quality. **Bone materials** (such as Hydroxapatite) with **metal nanoparticles** (such as Pt, Ag, Au) for medical diagnostics, **printed electronics materials** (such as ITO, QD’s), **functional lubricants** (such as sulphides), **ceramic and catalysts nanoadditives** for polymers (such as TiO_2, and SiO_2), **doped luminescent ceramics** (such as YAG:Ce), **superhydrophobic materials** (such as CeO_2 and SiO_2), and **functional polymer additives** (e.g. UV resistant materials like ZnO and flame retardants).

Continuous hydrothermal synthesis is still in its infancy, in terms of the scope of materials that can be produced and the control over particle size and shape. The project also allowed researchers to specifically focus on expanding the ‘repertoire’ of the process. Partners were able to demonstrate how metals, mixed metal oxides, sulphides, perovskites, phosphates and even metal organic frameworks could be produced. In addition to simple ‘production’, much of the work was around how the size and shape of the products themselves could be altered by changing process variables e.g. pressure, temperature, flow, concentration and precursor type. Most of this work is now published, with a significant number of publications in preparation.

SHYMAN PROJECT RESULTS AND HIGHLIGHTS

This section shows some of the highlights and technical breakthroughs for each of the key objectives for the SHYMAN project.

I. **Scale Up** – from reactor modelling to chemical engineering designs to the final plant (Figure 1)
II. **Formulation and Weight Loading** – increasing the weight loadings of the products and formulating them for use in target applications
III. **Sustainability and Production Cost –** proving that the SHYMAN process is a highly sustainable alternative and an economic opportunity for the nano-enabled market
IV. **New Materials, Metrology and Development** – increasing the scope of the process to manufacture an even wider portfolio of materials
V. **Dissemination and Engagement with Industry -** 7 case studies that demonstrate the performance and flexibility of the SHYMAN process in producing high quality nanomaterials

Figure 1 – the full scale SHYMAN plant

1. MODELLING AND REACTOR SCALE UP

Modelling was a crucial part of the project because it directly informed the design process for the scale up plant. The mixing regimes inside the reactor are crucial for the quality of the nanomaterials produced and to ensure that plant can operate continuously without blockages. Two different approaches were taken to understand mixing dynamics and how the mixing of the aqueous metal salt flow with the superheated water flow might be optimised at small scale, bench scale and full scale.

1.1 Pseudo Fluid Modelling

Continuous hydrothermal synthesis requires high pressures and high temperatures and therefore uses steel fittings and components, making visualisation of the flow mixing regimes impossible. However, visualisation is possible if transparent reactors seek to reproduce the mixing (mimicking the flow regime and flow ratios) but at ambient pressure and temperature. Figure 2 shows the initial 3D set up with cylindrical pipework in solid Perspex blocks. This process used sugar water to represent the denser (relatively) cold metal salt flow and methanol was used to simulate the less dense, super buoyant superheated flow. This approach allowed multiple flow rates and flow ratios to be observed and quantified. Dye was dissolved into the down flow (Figure 2b) to enhance the contrast between the two liquids and enable image analysis processing to quantify mixing efficiency.

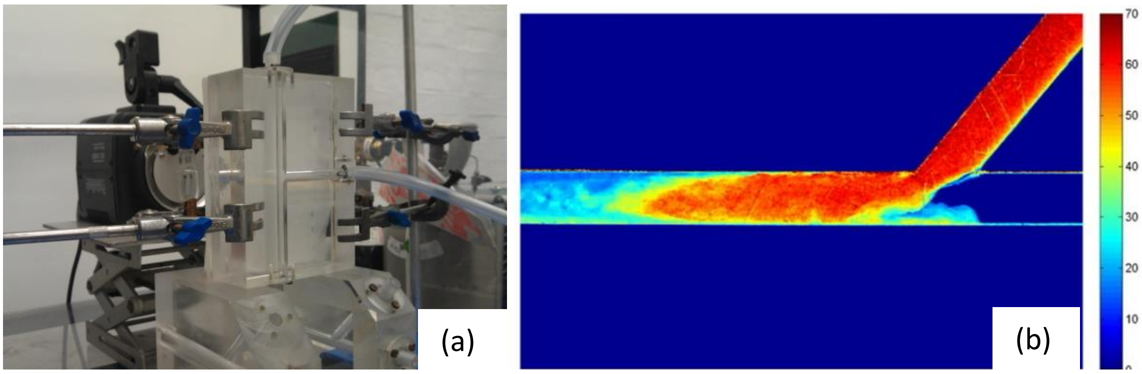
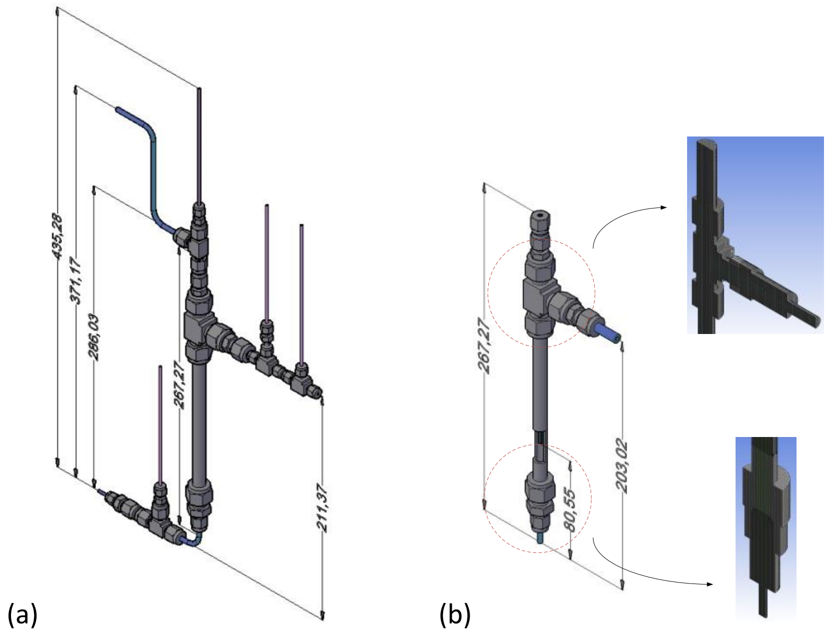


Figure 2 – (a) shows the experimental set up with the T arrangement (b) shows the quantified image of a Y piece showing the turbulent (but uneven) downstream mixing of the two flows

1.2 Computational Fluid Modelling

Figure 3 shows how the counter current reactor was virtually recreated for the computational fluid modelling. In order to produce a workable computational model the geometry was simplified slightly to the configuration indicated in Figure 3b. The cross-sectional images in Figure 3b also illustrate the mesh employed in the computations. The number of cells was carefully analysed and optimized for size, minimizing computational expense while assuring the results are mesh-independent.

Pseudo fluid modelling is one of several methods for directly visualising the flow dynamics in reactors which involve different mixing geometries.



(a)

(b)

Figure 3. Reactor dimensions along with details of the mesh employed (dimensions are in millimeters)

1.3 Final Validation of the Modelling Work

The models were all brought for validation and empirical work demonstrated that the models were indeed accurate. After this stage real nanoparticle samples were produced at bench scale and characterised carefully using HRTEM and additional image analysis tests to see how particle size was impacted by process conditions. Various process conditions were the simulated using the CFD and available kinetics data to create a predicted particle size distribution. These results can be seen in Figure 4.

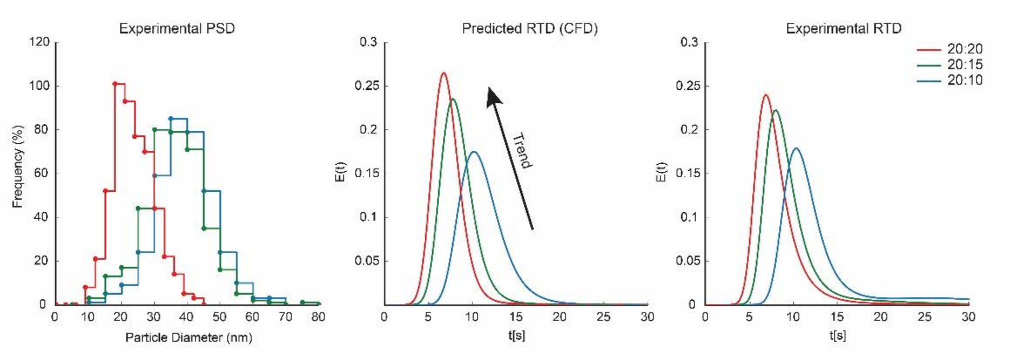


Figure 4. Experimental particle size distributions obtained for the production of hematite along with experimentally measured RTDs and predicted RTDs using the CFD code.

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2 PLANT DESIGN, ASSEMBLY, COMMISSIONING AND OPERATION

The process itself can be represented in the simplified block diagram shown in Figure 5a. This process was designed to operate under continuous conditions for a variety of inlet species and process conditions resulting in a wide range of potential products. Sustainability was optimised through water recovery (where possible), use of the most efficient heaters, and by minimising the consumed energy (using a heat recovery network). 5b shows the virtually rendered general arrangement layout of the plant.

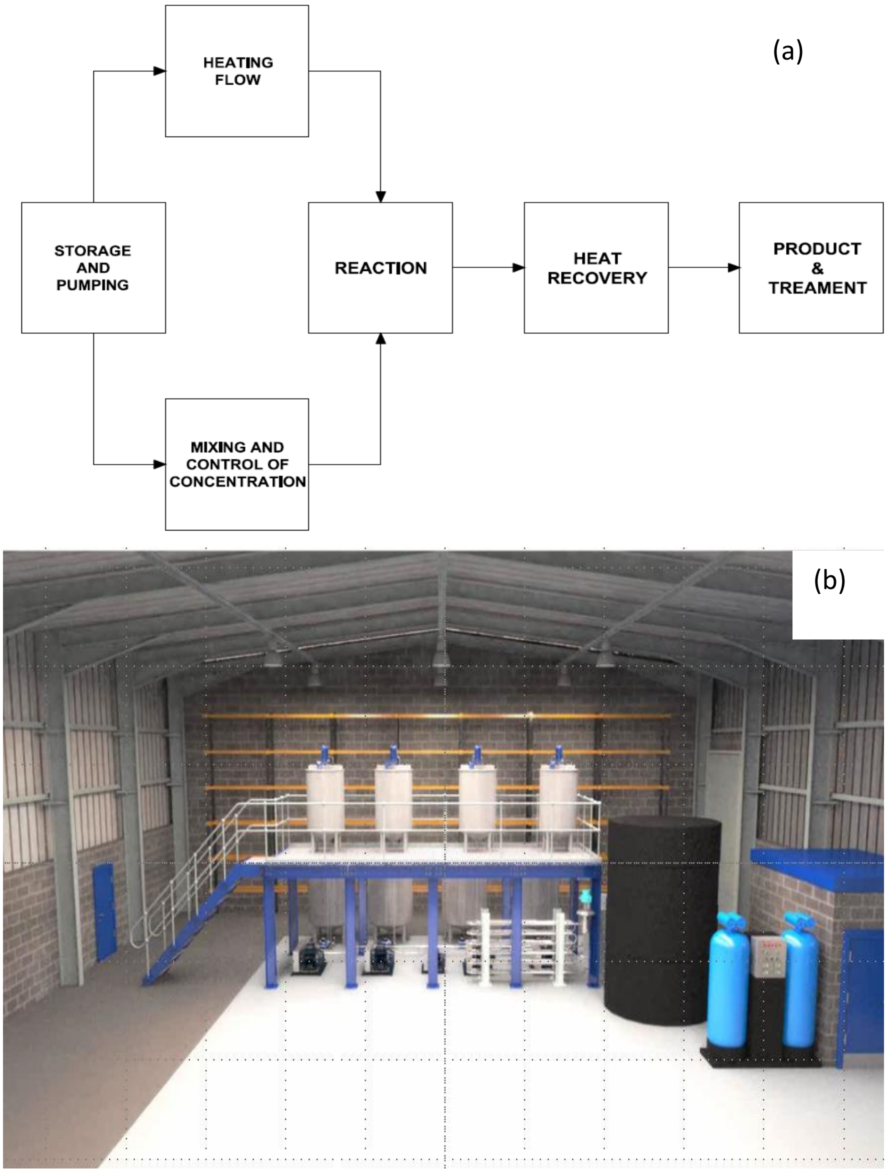


Figure 5 (a) shows the block diagram of the process (d) shows a virtual reconstruction of the general arrangement (GA)

3 SUSTAINABILITY MODELLING

Assessment of sustainability and impacts on the environment of SHYMAN technology was an integral part of the SHYMAN project. In the framework of this assessment Life Cycle Assessment (LCA) method has played a pivotal role alongside CCALC© which is a methodology specifically for calculating the CO_2 footprint of any given material or product. Life Cycle Assessment (LCA) is the most important analytical-information tool and allows users to assess the potential impacts product systems have on the environment throughout their entire life cycle.

LCA was applied in the SHYMAN project on two levels, defined by the extent or reach of the evaluated system. The first level provides "cradle to gate analysis" of the SHYMAN process, which means from the raw feedstocks to the final nanomaterial product. Figure 6 shows the general flowchart illustrating individual sub-processes (unit processes in LCA language) of the SHYMAN production process.

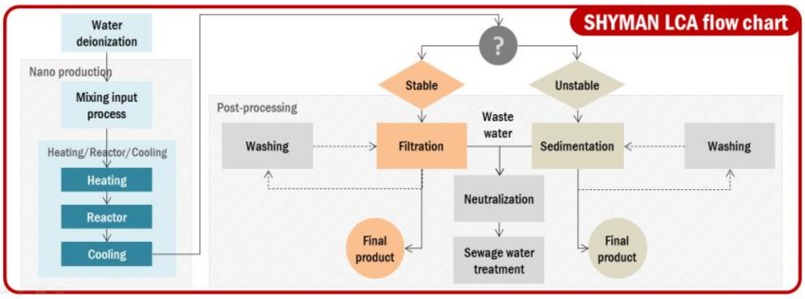
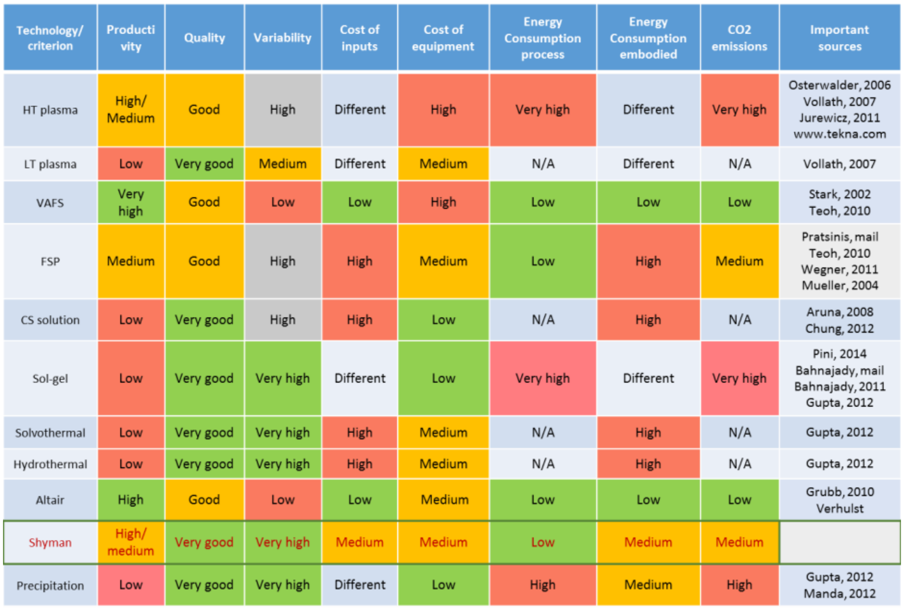


Figure 6 shows the SHYMAN production process for manufacture of the nanomaterials, with all stages prior to application

It should be pointed out that low variable technologies (e.g. sulphate and chloride process) have lower cumulative energy demand (CED) than the SHYMAN technology but in comparison with technologies with similar product flexibility (e.g. HT plasma, sol-gel…) the SHYMAN technology performs well in terms of CED and product quality. The same conclusion is valuable for Global warming potential (GWP). Figure 7 shows a conceptual comparison between different nanomanufacturing technologies as assessed from literature sources. In general SHYMAN process has many advantages and overall has one of the lowest environmental burdens (when the best precursors are chosen).



Technology/ criterion	Productivity	Quality	Variability	Cost of inputs	Cost of equipment	Energy Consumption process	Energy Consumption embodied	CO2 emissions	Important sources
HT plasma	High/ Medium	Good	High	Different	High	Very high	Different	Very high	Osterwalder, 2006 Vollath, 2007 Jurewicz, 2011 www.tekna.com
LT plasma	Low	Very good	Medium	Different	Medium	N/A	Different	N/A	Vollath, 2007
VAFS	Very high	Good	Low	Low	High	Low	Low	Low	Stark, 2002 Teoh, 2010
FSP	Medium	Good	High	High	Medium	Low	High	Medium	Pratsinis, mail Teoh, 2010 Wegner, 2011 Mueller, 2004
CS solution	Low	Very good	High	High	Low	N/A	High	N/A	Aruna, 2008 Chung, 2012
Sol-gel	Low	Very good	Very high	Different	Low	Very high	Different	Very high	Pini, 2014 Bahnajady, mail Bahnajady, 2011 Gupta, 2012
Solvothermal	Low	Very good	Very high	High	Medium	N/A	High	N/A	Gupta, 2012
Hydrothermal	Low	Very good	Very high	High	Medium	N/A	High	N/A	Gupta, 2012
Altair	High	Good	Low	Low	Medium	Low	Low	Low	Grubb, 2010 Verhulst
Shyman	High/ medium	Very good	Very high	Medium	Medium	Low	Medium	Medium	
Precipitation	Low	Very good	Very high	Different	Low	High	Medium	High	Gupta, 2012 Manda, 2012

Figure 7 a comparison of nanomanufacturing methods with a breakdown of each environmental impact/cost (HT plasma – High Temperature plasma synthesis LT plasma - Low Temperature plasma synthesis VAFS – Vapour-fed Aerosol Flame Synthesis FSP – Flame Spray Pyrolysis CS – combustion synthesis

A second, wider level of study was carried out to provide a wider scope with "cradle to grave" LCA for selected product applications of nanomaterials. Besides CED and GWP, other criteria were defined for overall multi-criterion qualitative comparison of various production technologies. From the comparison matrix in Figure 7 the SHYMAN has high productivity, high quality, multiple material, medium/low costs and low consumption of process energy. The ability of the SHYMAN process to produce large volumes of multiple types of high quality nanomaterials at a reasonable cost makes this technology highly competitive on the market.

4 CASE STUDIES

6.1 Healthcare

The aim of WP4 Case Study 1 was to investigate the potential of the nano-hydroxyapatite (nHA) manufactured using hydrothermal synthesis for healthcare applications. In particular, the focus of this case study was to use nHA in the manufacture of synthetic bone graft substitutes in paste and block form. It was concluded that the pastes demonstrated potential for use in bone repair although further investigation would be needed to take this product forward prior to commercial production. *The compatibiligy of the HA in medical applications*

A second healthcare related case study manufactured samples of Platinum (Pt), Silver (Ag) and Gold (Au) nanoparticles which were then structurally characterised. The most promising samples were taken forward for *in vitro* cell testing. It was found that the Ag NPs were not toxic to these cells under the conditions tested. *This means that the materials would be compatible potentially with medical imaging applications.*

6.2 Printed Electronics

A range of different materials for various aspects of printed electronics were tested within this Case Study including various sulphides and other semiconductors such as Indium Tin Oxide (ITO) for the application of transparent electrodes. Here, promising sheet resistance values were obtained. Final tests focussed on the use of Zirconium Dioxide (ZrO_2) for use in transparent coatings with a high refractive index. It was found that all samples produced transparent and homogeneous coatings, indicating that no particle agglomeration had occurred.

6.3 Enhanced Polymers

Initial tested focussed on introducing nanomaterials into polyurethane foams prior to the foaming process by dispersing nanoparticles into polyols. It was found that, by using a silane capping agent on the NPs, dispersions of SiO_2 particles into the polyol could be achieved. SiO_2 particles were also investigated in alternative polyols. Homogeneous stable dispersions of nano-ceramics in polymers were also achieved.

6.4 Optical Devices

This case study focussed on the potential use of nanomaterials with photoluminescent properties for use in car headlights. The aim in this study was to produce nanopowders which emitted visible light covering the entire white light spectrum, when excited with light in the UV range. The most promising result was found for Europium-doped ZrO_2 particles, where emission in the visible light range was detected. Nevertheless, the emission intensity was still lower than that of commercial phosphors although the solution was through the sintering of the SHYMAN materials to create larger clustered particles from the initial product.

6.5 Coatings

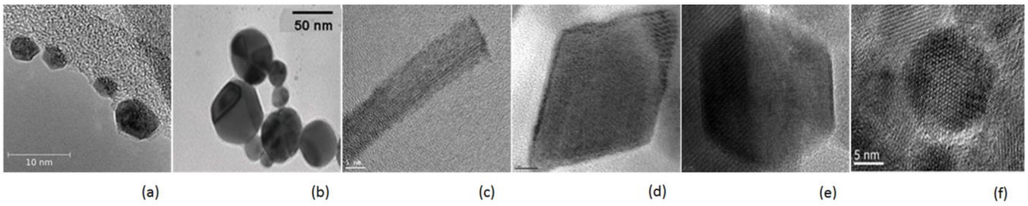
This Case Study looked into the introduction inorganic nanomaterials into PVDF paints to increase the hydrophobicity, in order to produce self-cleaning coatings for architectural surfaces (e.g. bridges, building facades). The most promising results were observed for surface-treated ZnO particles which were thermally stable and significantly improved the water contact angle of the paint, so were tested under weathering conditions. The weathering data showed no significant changes to the gloss or colour of the paint after 5000 hours of UV and humidity exposure (simulated in a weatherometer).

A final polymer based case study introduced nanomaterials into polypropylene (PP) to produce nanocomposites which have enhanced flame-retardancy or UV-resistance properties, for use in vehicle dashboards. The most promising results for UV-resistance was found to result from a doped nanoceramic and. In the case of flame retardancy, Mg-Al-CO_3 LDHs was added into PP and the burn rate improved by over 50 % compared to blank PP.

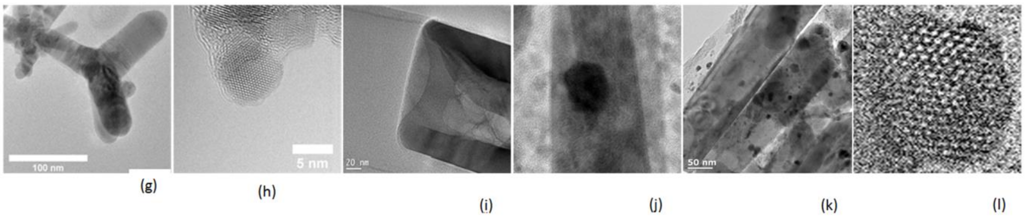
7 NEW MATERIALS DEVELOPMENT

The SHYMAN project also provided the opportunity to create new materials using continuous hydrothermal and solvothermal synthesis. The main objective of this activity was to increase the scope or potential impact of the process by increasing the scope of range of materials that were possible through the technology. The list below (with some examples in Figure 8) shows materials been made (for the first time) using continuous hydrothermal/solvothermal routes.

I. Sulphides – including CdS, CuS, FeS_2, PbS, Bi_2S_3, ZnS and MoS_2
II. Metal Organic Frameworks – including ZIF8, MIL53, MIL101, HKUST-1, NOTT300 UiO-66.
III. Mixed metal oxides – $BaTiO_3$, $Sr_xBa_{1-x}TiO_3$,
IV. Doped Metal Oxides - Co-TiO_2, Ni-TiO_2
V. Phosphates – including $LiFePO_4$, $LiMnPO_4$
VI. Layered double hydroxides – including Ca_2Al-NO_3, Mg_3Al-C3O, Mg2Al-CO_3, Co_3-Al-CO_3, Co_3-Al-NO_3, Hybrids, TiO_2@Mg_2Al-CO_3, TiO_2@Co_2Al-CO_3, Co_3O_4@Mg_2Al-CO_3
VII. Metals – including Ag, Pt, Pd, Au, Ni, Cu



(a) Au (b) Ag (c) WO_3 - *scale bar is 5nm* (d) iron oxide (Fe_2O_3) - *scale bar is 5nm* (e) $BaTiO_3$ - *scale bar is 2nm* (f) $ZnFe_3O_4$



(g) CdS (h) ZnS (i) $Ca_{10}(PO_4)_6(OH)_2$ (j) Ag inside sheet of $Ca_{10}(PO_4)_6(OH)_2$ - *scale bar is 5nm* (k) Pt on TiO_2 nanotubes (l) Ni MOF-74 - *scale bar is 5nm*

Figure 8 – examples of nanomaterials made during the SHYMAN project.

8. IMPACT ASSESSMENT

> “Nanotechnology's potential is vast and it's real. The opportunity for nanotechnology ranges from improving Olympic sports equipment to discovering better treatments for Alzheimer's disease. But our ability to reap the long-term benefits of nanotechnology -- in areas from energy production to medicine -- will depend on how well industry and government manage the safety and performance of this first generation of products.” ***Dr. Andrew Maynard*** *-Chief Science Advisor to the Project on Emerging Nanotechnologies, and Science Advisor to the Synthetic Biology Project at the Woodrow Wilson International Centre for Scholars.*

The main aims of the SHYMAN project were to;

A. **Scale up the continuous hydrothermal process** – *the output has increased 1000x from the pilot reactor scale.*

B. **Reduce the CO_2 footprint** – *LCA has shown the process to be highly sustainable compared with alternative technology*

C. **Reduce processing costs** - *the process can now operate and produce a 10wt% solution continuously and manufacture at approximately 5 euros per kilo*

D. **Create new materials** – *the materials portfolio has increased to include, metals, metal sulphides, metal organic frameworks and hybrid nanomaterials.*

E. **Increase efficiency of application** - *decreasing the need for excess nanomaterials with high dispersion rates*

F. **Improve nanomanufacturing safety** – *toxicology results are excellent, product formulation has been established to allow liquid dispersions to be maintained during processing, thus avoiding the need for handling of any dry powders.*

Figure 9 shows the ambitions of the SHYMAN project at the conceptual stage, back in 2010. The aim was to extend a proven platform technology (at bench scale) in the form of continuous hydrothermal synthesis and scale the process to industrial scale. This scale would have to be a minimum of 100 tons per annum to demonstrate industrial relevance. The figure shows the increasing reach (dotted line) pushing a high value low volume process into the industrial region (nominally low value and low quality) by creating a high quality lower value proposition. *This figure has been amended to show where the SHYMAN plant positions the technology in the market place.*

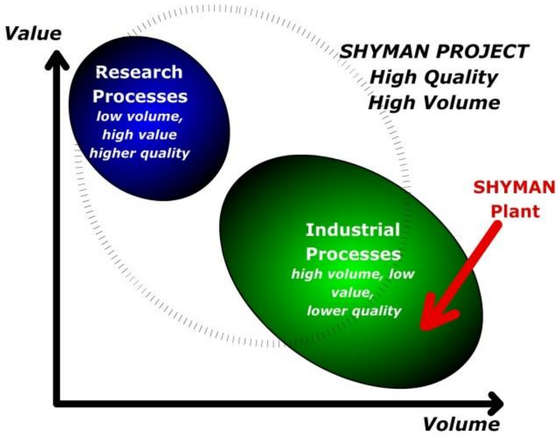


Figure 9 – The change in scope for continuous hydrothermal synthesis from a lab based technology to an industrial scale process

The impact on the market made possible by the SHYMAN project, will be seen over the next 3-5 years as commercial production begins. Commercial operation was clearly not possible during the lifetime of the project, but the ability of the process to manufacture materials that are relevant to diverse market sectors now provides a significant opportunity. The production of metals, metal oxides, sulphides, phosphates, hydroxides, carbonates, metal organic frameworks all prove that the process is a platform technology. As an example of future growth, Promethean Particles has estimated a 2 fold increase in staff in the next 18 months as a result of the SHYMAN project. The use of case studies has also shone a spotlight on the opportunities in markets that include: healthcare – through diagnostics and bone materials; printed electronics – through conductives, semi-conductives and high refractive index materials; polymers – through flame retardant, scratch proof materials; photonics – through luminescent materials; coatings and lubricants – through UV resistant and superhydrophobic materials.

SHYMAN has indeed had an impact on the SMEs within the consortium, from two significant aspects: **Internally**, the access to the network of excellence of the main partners in the project allowed these small companies to be in direct contact with the most advanced developments and knowledge in the field; the potential gains -both tangible and intangible- could not be expected by the sum of all the individuals partners activity. **Externally**, partnering such a relevant consortium has added value to all 7 SME's. Each SME has been able to promote their involvement in the project this increasing the confidence any third party could request for our capability of managing complex projects. Both aspects are really difficult to achieve for a spin-off company with no track record as an organization. Also, in essence participating in this project has placed many of the SMEs on the map of European nanotechnology research.

Since the SHYMAN plant has an output of over 1000 tons per year, then it will remain the world's largest continuous hydrothermal plant indefinitely. As such, the SHYMAN project has placed an EU consortium at the forefront of world nanomanufacturing and given the technology sufficient traction to create considerable global interest. This has generated EU jobs in an emerging market place where new IP generation (around the process and products) now form a strong platform for global manufacturing. **The SHYMAN project has enabled the technology to be scaled to an industrially meaningful level whilst demonstrating that it is a low cost, high quality alternative to existing nanomanufacturing processes. As a result, the SHYMAN project has guaranteed EU jobs and not just income for EU companies.**

As mentioned above, the scope or reach of the technology means that many materials and products can be made using nanomaterials from the SHYMAN plant. Figure 10 shows examples of market sectors that have direct societal implications, from cancer therapies to sunscreens and enhanced fabrics to flexible electronics. All these market sectors impact on society on a daily basis. The most significant impact of the SHYMAN project is probably the creation of a new industrial scale plant that can create high quality nanomaterials using a highly sustainable process i.e. using water as a solvent, high levels of recycling ad with very efficient heat recovery. All of these aspects make the process and the plant environmentally sound for a society that desperately needs to 'do more but use less'.

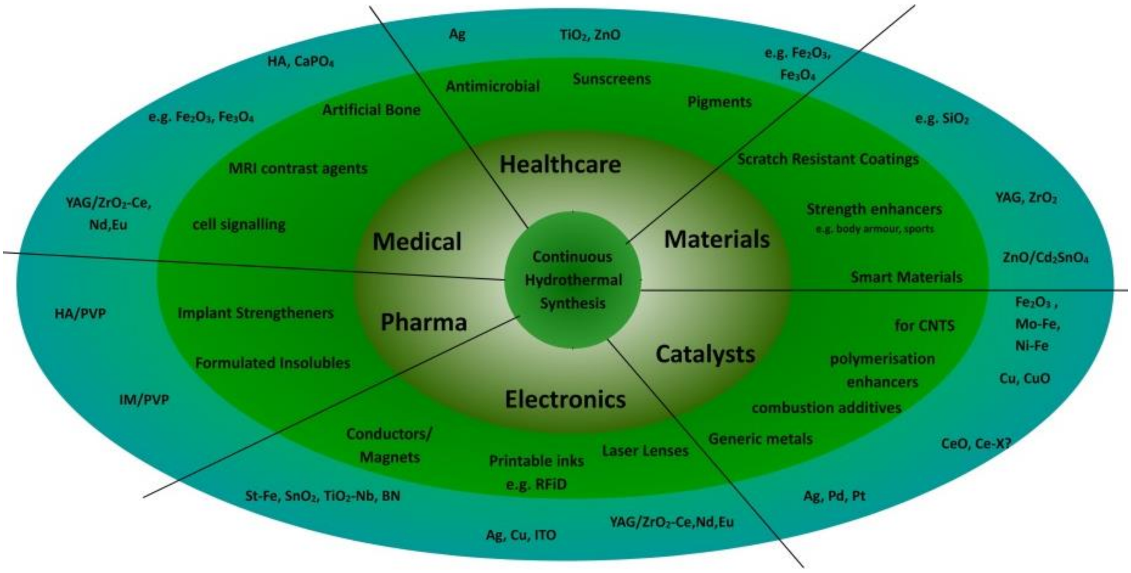


Figure 10 - schematic sowing the scope and reach of nanomaterials in various market sectors

The use of the case studies within the SHYMAN project has been an effective means to assess and create impact within the business community. Each case study has allowed key nano-enabled markets to be evaluated and a plan of action to be established. The creation of the plant itself has created considerable interest and curiosity outside the project within the business community. The end of the project has seen more engagement with these potential end-users.

During the course of the project we estimate that over 1000 students (chemists and chemical engineers) have engaged with the SHYMAN project through workshops, lectures, and design tasks relating to the design of the full scale process. Figure 11 shows undergraduate chemical engineers standing on the SHYMAN plant gantry mid-way through construction.

Figure 11 Second year chemical engineers visit the plant under construction December 2015 as part of their course at Nottingham.

A week long summer school was run in May 2014 at the University of Valladolid attended by 31 participants from 9 countries. 18 lecturers from 6 different countries attended and presented at the summer school (Figure 12). *Some attendees actually went on to take up positions as interns, placement students and were involved in the SHYMAN project directly as researchers.*

Figure 12 - the participants and lecturers at the SHYMAN summer school May 2014

CONCLUDING REMARKS

"The SHYMAN project will establish continuous hydrothermal synthesis as one of the most flexible and sustainable means of manufacturing nanomaterials on a large scale, serving industries of strategic importance to Europe."

This was the opening paragraph of the SHYMAN proposal in April 2011

We have succeeded in this ambitious project with the design, build and operation of the world's largest multi-material continuous hydrothermal plant in the world. This plant is capable of making high quality nanomaterials including metals, metal oxides, hydroxides, solid solutions, carbonates, sulphides as well as more complex nanoporous materials including MOFs, ZIFs and COFs. This project has only been possible through the close collaboration of 18 partners across Europe with world-class expertise in numerous disciplines including chemical engineering, chemistry, physics, life cycle assessment and materials engineering.

Many of the case studies have shown that the process can produce nanomaterials with a clearly defined technical and economic edge in the marketplace. Many new nanomaterials have also been produced using this platform technology.

It has been proven to be a flexible, economic and environmentally sustainable technology with the capacity for scale up, well beyond lab scale to full industrial scale production.