



PrometheanParticles



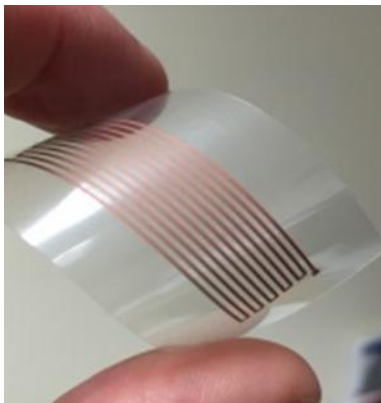
Formulating solutions with nanomaterials

**Commercialisation of Nanomaterials – Commissioning a new
Nanomaterial plant**

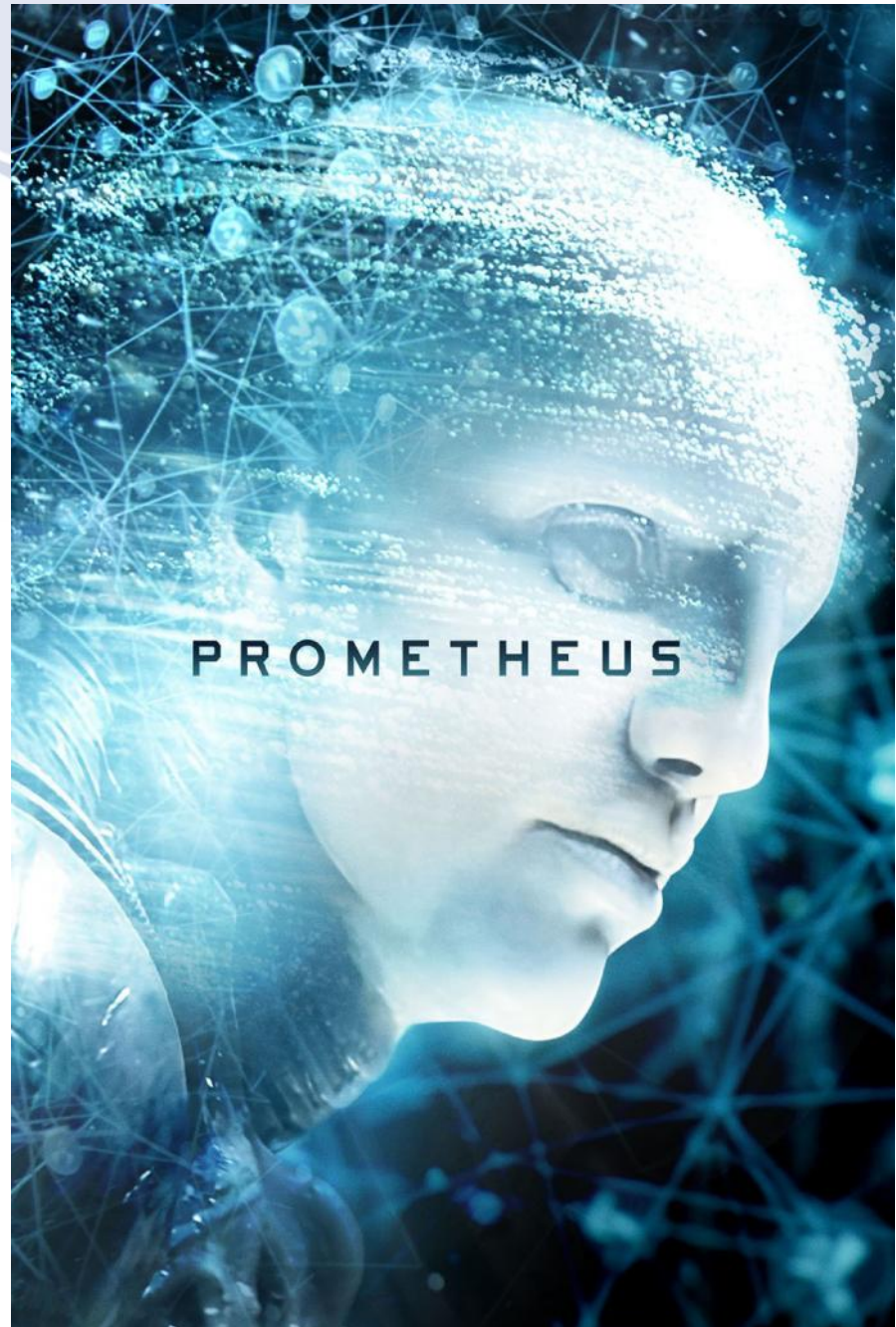
7 June 2017, Burlington House, London.

Overview

- Introduction to Promethean and CHS technology
- What we (can) do and what markets do we access? (not too salesy!)
- A sustainable scale manufacturing process
- Overcoming the Hurdles for success



Prometheus?



Prometheus?



**In Greek mythology
Prometheus is a Titan
known for his wily
intelligence, who stole
fire from Zeus and gave
it to mortals for their
use...**

Prometheus?

....let's hope we have a somewhat happier ending!



Promethean Particles

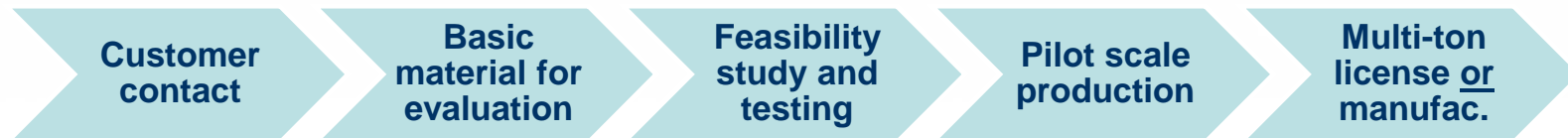
Design, develop and manufacture inorganic nanomaterial dispersions

- Founded 2007
- Newly refurbished facility containing labs and commercial scale manufacturing
- 11 FTEs
- Nottingham, UK



Business Model

Design, develop and manufacture inorganic nanoparticle dispersions for a range of industrial customers.



Target customers are global leaders in their market including:

- application specific end-users and
- strategic partners with multiple needs such as chemical companies
- customer can own foreground IP for the material in their application

Promethean offers:

- **Manufacturing capabilities up to multi-ton scale**
- **Sale of reactors for client's manufacturing under license at any scale**

Technology



**NANOPARTICLE
PRODUCTION**



**COMMERCIAL
APPLICATIONS**

**DRY
SYNTHESIS
METHODS**
Plasma, flame, laser

FORMULATION
Redispersion, surface
modification

**WET SYNTHESIS
METHODS**
Sol-gel
Hydrothermal
Solvothermal

**CATALYSTS
COMPOSITES
MEDICAL
COSMETICS
ELECTRONICS
HEALTHCARE
MATERIALS
POLYMERS**

Continuous hydrothermal synthesis...

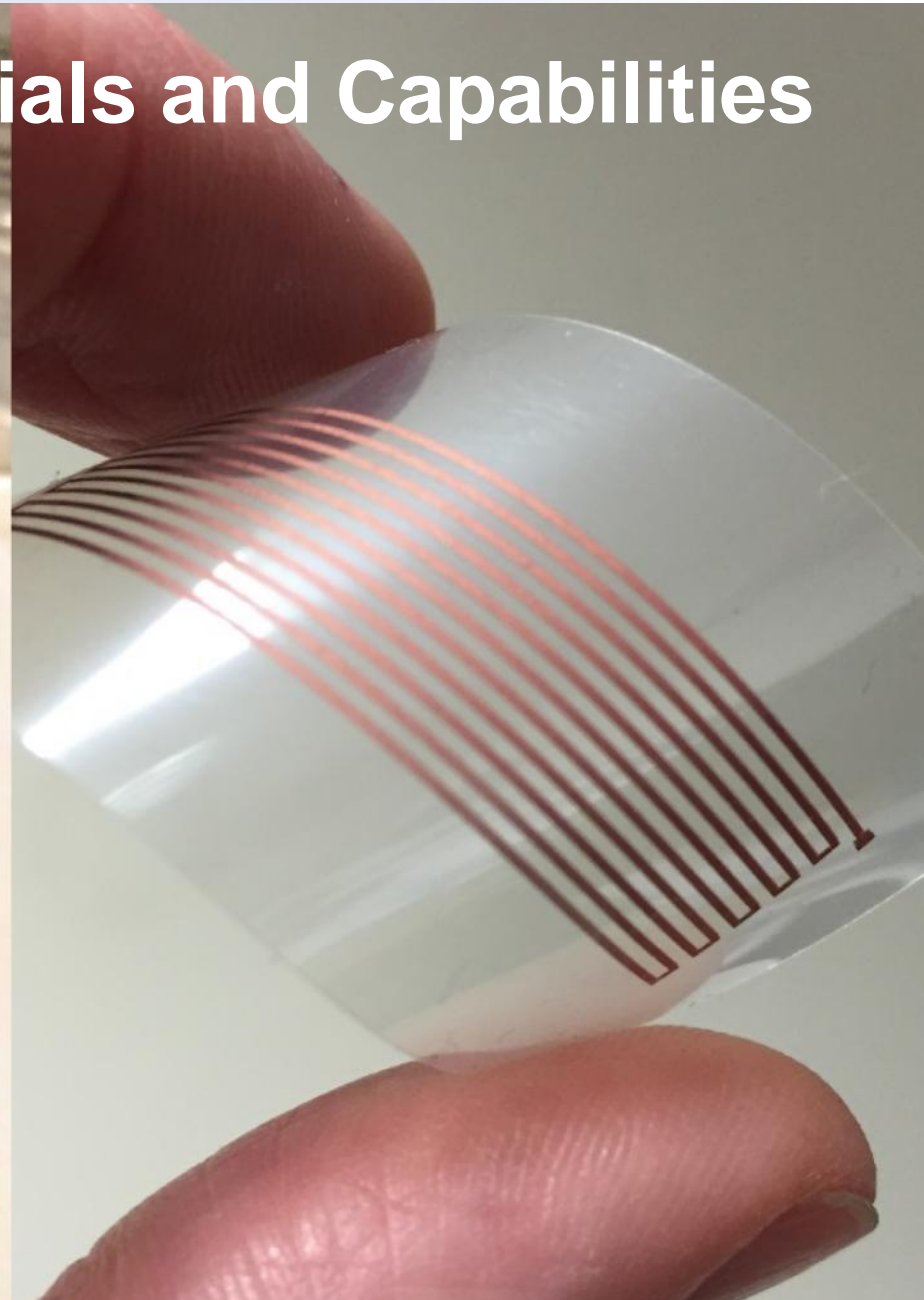
- Inorganic nanomaterials produced in hot water (solvent)
- Not airborne – no inhalation/explosion risk of fine powders ✓
- Product is dispersion-based – reduced agglomeration, ease of formulation and use in liquid application ✓
- Long term product stability without deterioration ✓
 - e.g. oxidation of metallic nanomaterials
- **Continuous** – facile scale up with low capital and operating costs ✓



For an animation showing the Promethean counter-current process, please visit

<http://www.prometheanparticles.co.uk/our-technology/>

Materials and Capabilities

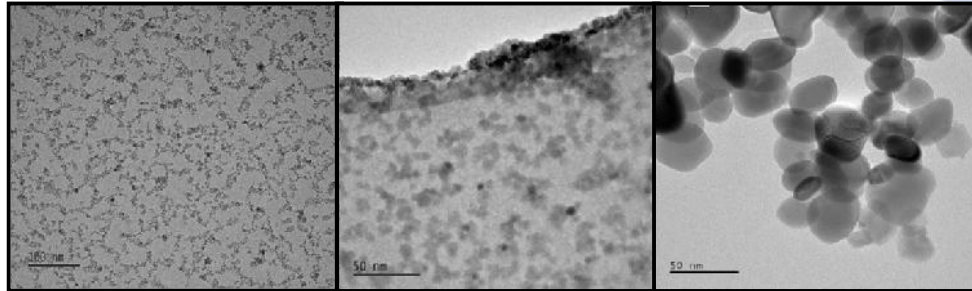


Chemistries explored to date

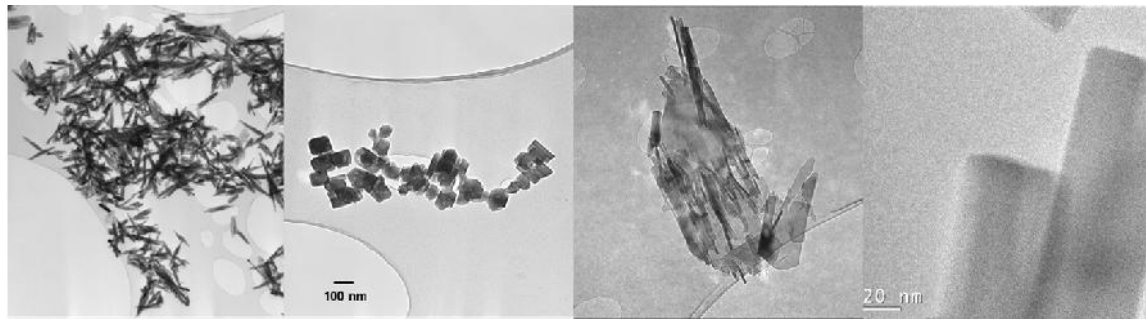
- Metals... Ag, Pd, Pt, Au, Cu, Ni
- Metal Oxides... ZnO, ZrO₂, TiO₂, CeO₂, CuO, FeOx
- Mixed Metal Oxides... Ce_{1-x}Zr_xO₂, IZO, ITO
- Complex Oxides... BaTiO₃
- Sulfides... CdS, ZnS, PbS, MoS₂
- Hydroxides... Al(OH)₃, Mg(OH)₂
- Oxyhydroxides... AlO(OH)
- Phosphates... LiFePO₄, hydroxyapatite,
- MOFs... HKUST-1, Ni-74

Promethean offer contract development of bespoke materials in partnership

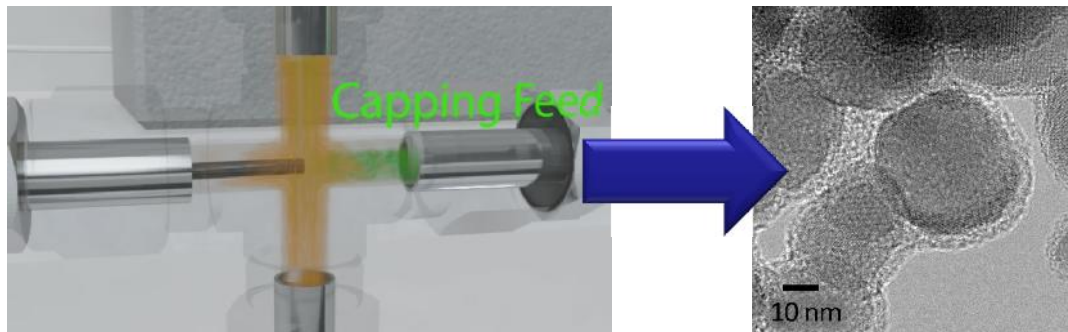
Capabilities



Size control
e.g. Hematite 5-50 nm



Morphology control
e.g. hydroxyapatite



Surface functionalisation
e.g. dextran-coated magnetite

Application areas

Printed Electronics

- Conductive inks
- Semiconductors
- Dielectrics

Nanocomposites

- Flame retardants
- Functional coatings

Healthcare

- Bone scaffolds
- Diagnostics
- Contrast agents

Green Energy

- Batteries
- Photovoltaics
- Adsorbents

Catalysis

- Precious metals
- Ceramics

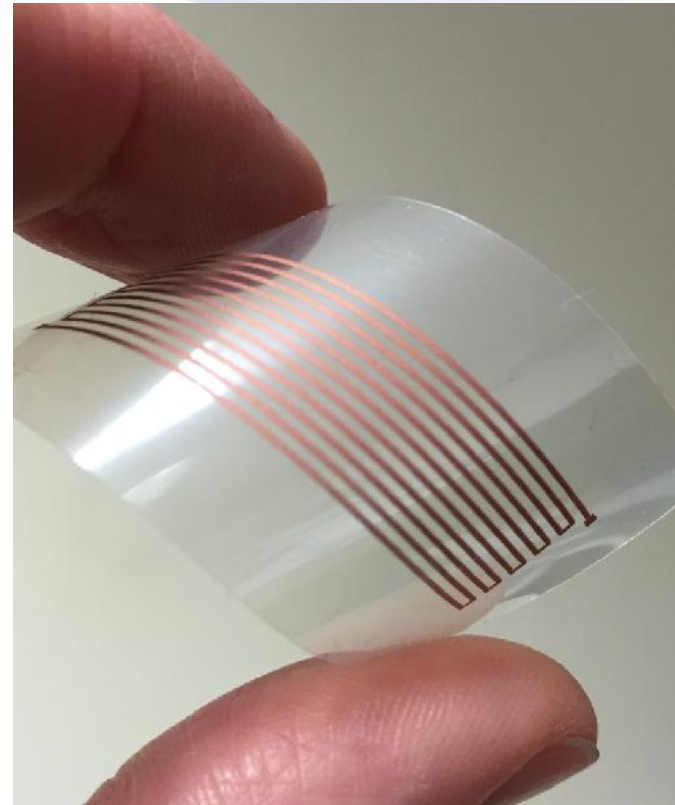
Nanotechnology - enabling Printed Electronics?

Conductives

- Printed conductive tracks
- Ultrafine features
- Low temperature sintering enables flexible substrates

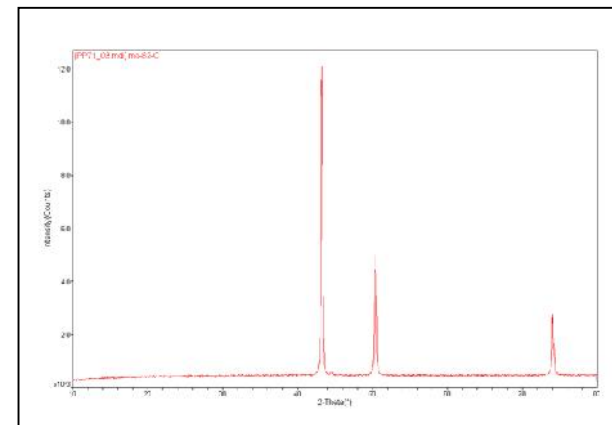
Semiconductors, dielectrics

- Printed components
- E.g. transistors, capacitors
- Roll to roll deposition enables mass production



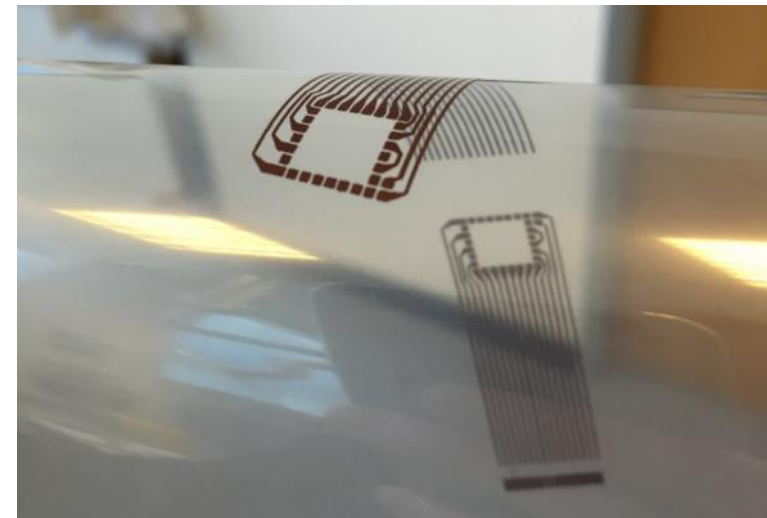
Copper

- Conductive metal NPs
- Cost-effective alternative to Ag
- Contains only Cu and an antioxidant
- Cost-effective process due to low CAPEX and OPEX costs
- Scale-up of continuous production achieved (multi-kg batches)
- **Non-oxidised material, up to 60 wt% Cu available in a range of solvents**



Copper inkjet ink

- Formulated through an integrator partner
 - 30-35 wt% Cu metal
 - Film thickness $<1\ \mu\text{m}$
 - Sintering:
 - Photonic, laser or thermally sintered under N_2 .
-
- **Unique product in the PE market**
 - **Good conductivity on all substrates**
 - **3D printing of conductive tracks**



Economics and scale-up





Bench-scale reactor (g/hr)

Rapid prototyping of the optimised solution is developed at the bench-scale

Pilot-scale production (1-10 tons per year)

Excellent scale-up
reproducibility





SHYMAN project

EU FP7 project on scale up and developing industrial products

Approx €10M over 4 years

May 2012-2016

Includes scale up to 1000 ton per year, located at a manufacturing site in UK

Estimated plant on-line early 2016

**‘Sustainable Hydrothermal
Manufacturing of Nanomaterials’
SHYMAN**

shyman



Infinity Series - 1,000+ tons/yr

Scale of Manufacture

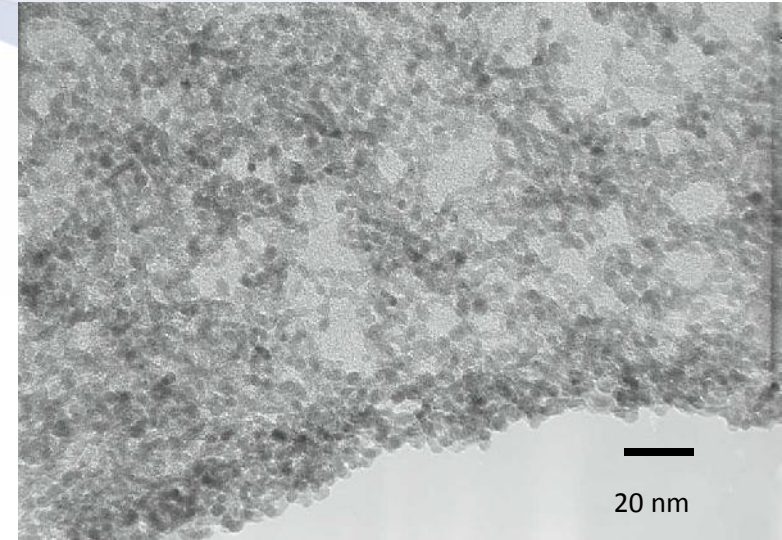
- Scale-up highly cost effective
- Customer can license technology for manufacture at their own site
- Potential for Promethean to manufacture
- Low energy and water costs
- Equipment costs
 - Continuous process requires low capital expenditure and scales easily
 - Build cost was comfortably contained within the project budget

Commissioning process

- Full commissioning had not been completed under the project timeline
- Pressure Systems Safety Regulations adherence
- Up-rating of utilities – gas, water, electricity
- Waste treatment system commissioning
 - Trade effluent notice application
- Procurement of additional auxiliary equipment
 - E.g. racking, materials handling pumps etc.
- Selection of model reaction(s)
- Procurement of intermediate quantities of precursors

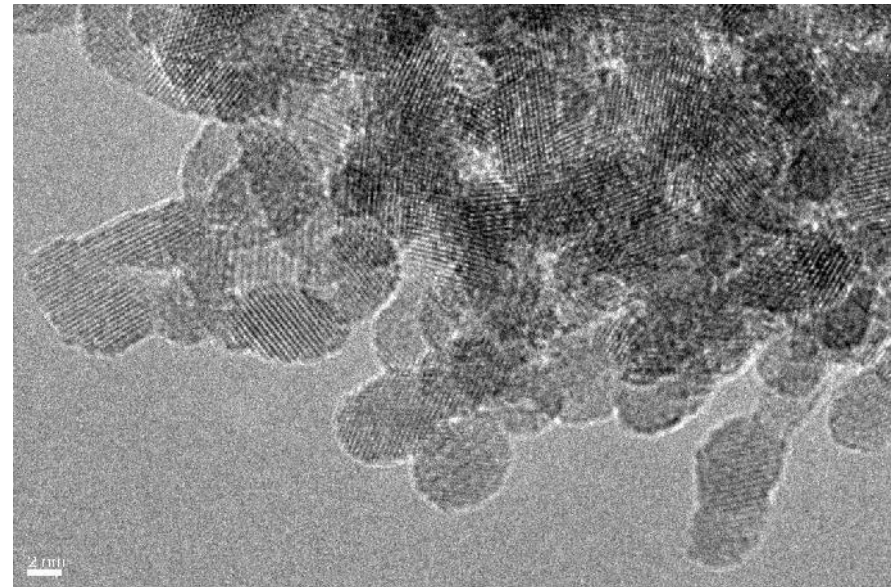
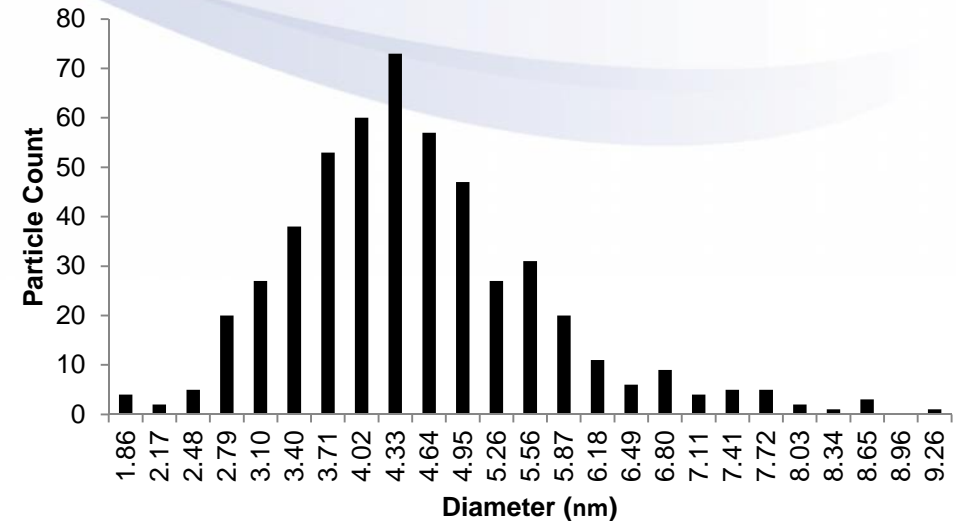
Model reaction: Zirconium dioxide

- Refractory ceramic
- High transparency
- Aqueous dispersion shown here
 ZrO_2 @ ~10 wt%
- Pilot-scale reaction can produce
~500 g/hr
- Transparent coatings and barrier
layers



Model reaction: Zirconium dioxide

- Excellent reproducibility
- High transparency up to 10 wt%
- Production rate 1500-2000 L/hr
- 100-1000 Tpa dry weight equivalent.
- Dispersed product output would be much higher
- Product available for sale



Uni spin-out opens world's largest nanoparticle plant

Posted on 13 Jul 2016 by Jonny Williamson



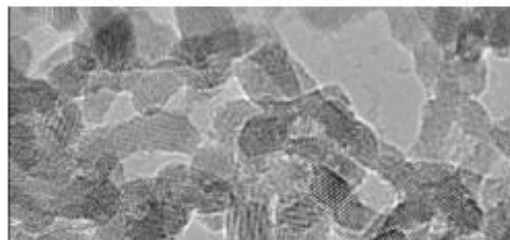
Professor Ed Lester at the Promethean Particles nanomaterials plant - image courtesy of University of Nottingham.

University of Nottingham spin-out business, Promethean Particles, has opened the world's first facility which is capable of producing thousands of different nanomaterials.

Nanoparticles are used for a variety of uses, such as in artificial bone; scratch proof coatings; printed electronics, and flame retardant materials.

The plant, which was developed as part of a pan-European nanomaterials research programme – known as SHYMAN – can manufacture more than a thousand tonnes of nanomaterials every year.

The SHYMAN (Sustainable Hydrothermal Manufacturing of Nanomaterials) project, which had a total value of €9.7m, included partner universities and businesses from 12 European countries.



ANNUAL MANUFACTURING REPORT 2017



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Case study

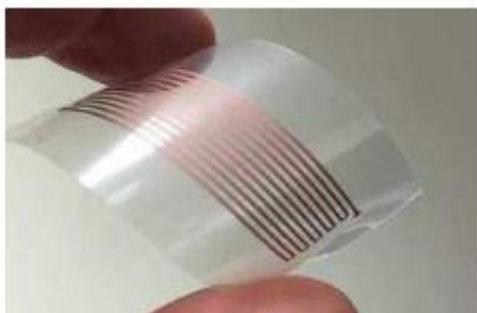
Promethean: nanoparticle products go into full-scale production

From: [Innovate UK](#)

Part of: [Horizon 2020: the EU research and innovation funding programme](#), [UK economic growth](#), [Research and development](#), [European funds](#), and [Business enterprise](#)

Published: 28 November 2016

Nottingham University spin-out builds on €10 million multi-partner EU project to enter global market in novel inks, paints and coatings.



Promethean is targeting specialist markets with nanoparticle products such as

Scaling up: a nanoparticle adventure



November 2016

Challenges



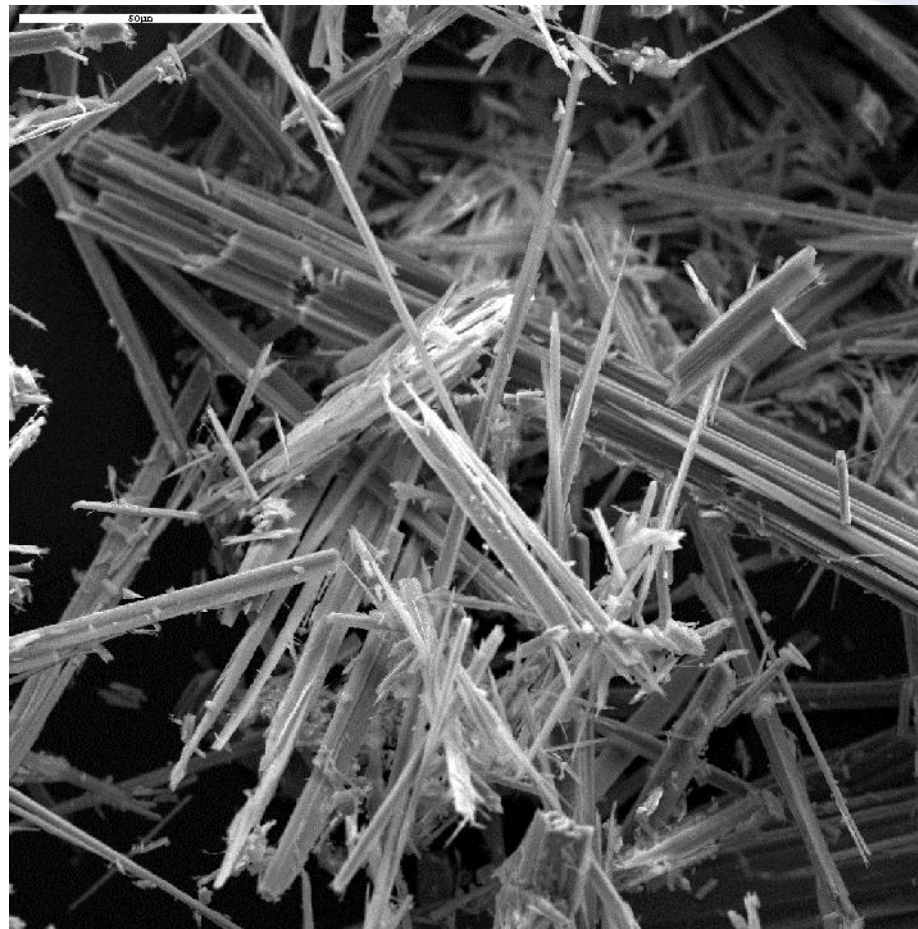
Hurdles (challenges?) to overcome

- Recessions
- Are nanomaterials toxic?

Are nanomaterials toxic?



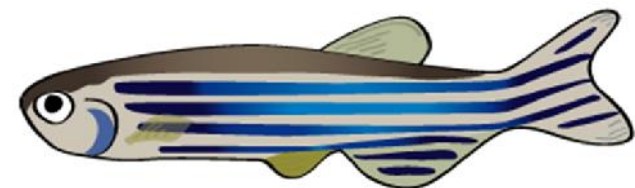
- What common material is this?



Interaction with EU Nanotox. projects



- NanoMILE (*Systematic investigations of the mechanisms and effects of engineered NanoMaterial Interactions with Living systems and/or the Environment*) – **FP7**
 - Safer-by-design approach to engineered nanomaterials
 - Ended Feb 2017
- NanoFASE (*Nanomaterial FAte and Speciation in the Environment*) – **H2020**
 - Persistence of nanomaterials in the environment
 - Started October 2015

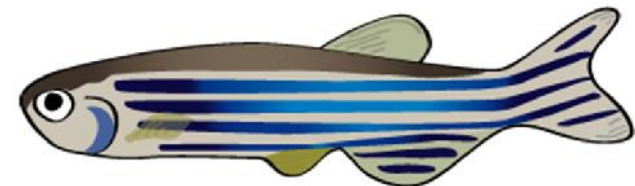


Interaction with EU Nanotox. projects



Some difficulties faced as a commercial NM producer:

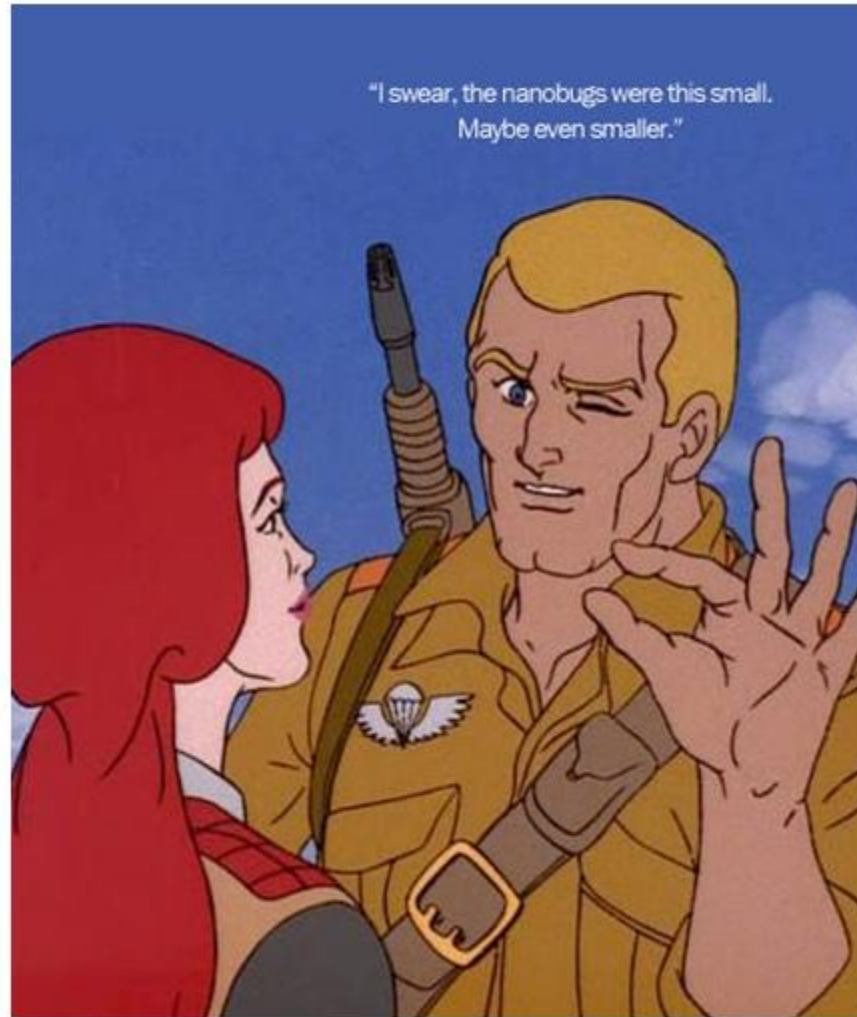
- Studies must focus on realistic exposure routes
- Toxicologists leading the project publish in toxicology journals
 - Negative toxicity results seem less desirable!
- Publishing reports about safe materials is equally important
- Chemical composition seems to be the major driver of toxicity
 - E.g. CdSe is toxic regardless of its size
- ‘Can we have this material at 105 nm please?’



Hurdles (challenges?) to overcome

- Recessions
- Are nanomaterials toxic?
- What is a nanomaterial anyway?

What is a nanomaterial?





European
Commission

ENVIRONMENT

European Commission > Environment > Chemicals > Nanomaterials >

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Q&A definition

Nanomaterials in REACH and CLP

Inventory

Combination effects of chemicals

Protection of laboratory animals

Persistent Organic Pollutants (POP)

Trade of Dangerous Chemicals

Questions and Answers on the Commission Recommendation on the definition of Nanomaterial



1. [WHY DO WE NEED A DEFINITION OF THE TERM "NANOMATERIAL"?](#)
2. [ARE NANOMATERIALS HAZARDOUS?](#)
3. [WHY NOT USE EXISTING INTERNATIONAL DEFINITIONS?](#)
4. [IS IT REALLY POSSIBLE TO HAVE ONLY ONE SINGLE DEFINITION?](#)
5. [WHY IS THE NUMBER DISTRIBUTION THRESHOLD PUT AT 50 % WHEN SCENIHR SUGGESTED 0.15 %?](#)
6. [WHY IS IT NOT SPECIFIED THAT ONLY MANMADE MATERIALS CAN BE NANOMATERIALS?](#)
7. [WHY NOT FOCUS THE DEFINITION ON NANO-SPECIFIC PROPERTIES INSTEAD OF SIZE, AS THIS IS DONE IN OTHER DEFINITIONS, INCLUDING SOME OF THE DEFINITIONS IN EXISTING EU LEGISLATION AND SOME DEFINITIONS IN NON-EU COUNTRIES?](#)
8. [WHY IS THE SIZE RANGE LIMITED TO 1 NM – 100 NM?](#)
9. [WHY MUST THE PARTICLE DISTRIBUTION BE MEASURED IN NUMBER AND NOT BY MASS WHICH IS COMMONLY USED?](#)
10. [ARE AGGREGATES AND AGGLOMERATES OF NANOPARTICLES NANOMATERIALS?](#)
11. [WHAT IS THE PURPOSE OF INCLUDING THE VOLUME SPECIFIC SURFACE AREA AS A METRIC?](#)
12. [WHY DOES THE DEFINITION ONLY COVER PARTICULATE MATERIALS AND EXCLUDE NANOSTRUCTURED MATERIALS?](#)
13. [WHAT ABOUT NANOMATERIALS IN PRODUCTS?](#)
14. [CAN THE DEFINITION BE USED WITHOUT MEASUREMENT AND STANDARDS BEING AVAILABLE?](#)
15. [WHY IS THE DEFINITION SO BROAD AND WHAT ABOUT ECONOMIC IMPACTS?](#)
16. [WILL THE DEFINITION BE SUBJECT TO FUTURE REVIEWS?](#)
17. [HOW WILL THE COMMISSION ENGAGE STAKEHOLDERS IN THE DEFINITION?](#)
18. [WILL THE COMMISSION PROPOSE NEW LEGISLATION ON NANOMATERIALS/REVISE EXISTING LEGISLATION?](#)
19. [WHY DID THE COMMISSION USE THE LEGAL INSTRUMENT OF A COMMISSION RECOMMENDATION, AND HOW WILL THIS BE IMPLEMENTED IN SPECIFIC LEGISLATION?](#)

1. WHY DO WE NEED A DEFINITION OF THE TERM "NANOMATERIAL"?

The definition will primarily be used to identify materials for which special provisions (concerning for example risk

Hurdles (challenges?) to overcome

- Recessions
- Are nanomaterials toxic?
- What is a nanomaterial anyway?
- Nanomaterial registries
 - Denmark, France, Belgium

European Union Commission Rejects Mandatory Nanomaterial Registry

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29 Apr 2016 --- Much to the dissatisfaction of research organizations and consumer groups, the European Commission appears to have rejected the proposed registry for the use of nanomaterials. The registry would have required those within the food and beverage industry to register any nanomaterials used in substances of products.

Recent investments in nanotechnology research by the United States Department of Agriculture demonstrate that nanotechnology's potential for food development and food safety is significant. Dr. Hongda Chen, National Program Leader for Bioprocess Engineering and Nanotechnology at USDA's National Institute of Food and Agriculture (NIFA) details several of those possibilities in the April/May 2016 edition of ***The World of Food Ingredients***. He says: "Such a fundamental science really has a significant impact on agriculture and food and many other industry sectors."

The EU's recent decision will allow companies to utilize nanomaterials without having to register them in a mandatory system. Several organizations, including the Bureau Européen des Unions de Consommateurs (BEUC, The European Consumer Organization) were campaigning for the introduction of a mandatory registry. However, instead of creating a registration system for the use of nanomaterials within any industry in the European Union, the Commission seems to have chosen for an observatory, which would only contain information which has been supplied voluntarily.



IT'S TOO EASY TO JUST SAY
"BREWED TEA"!

hot water and tea leaves,
these only are the right ingredien

THIS IS HOW WE DO IT

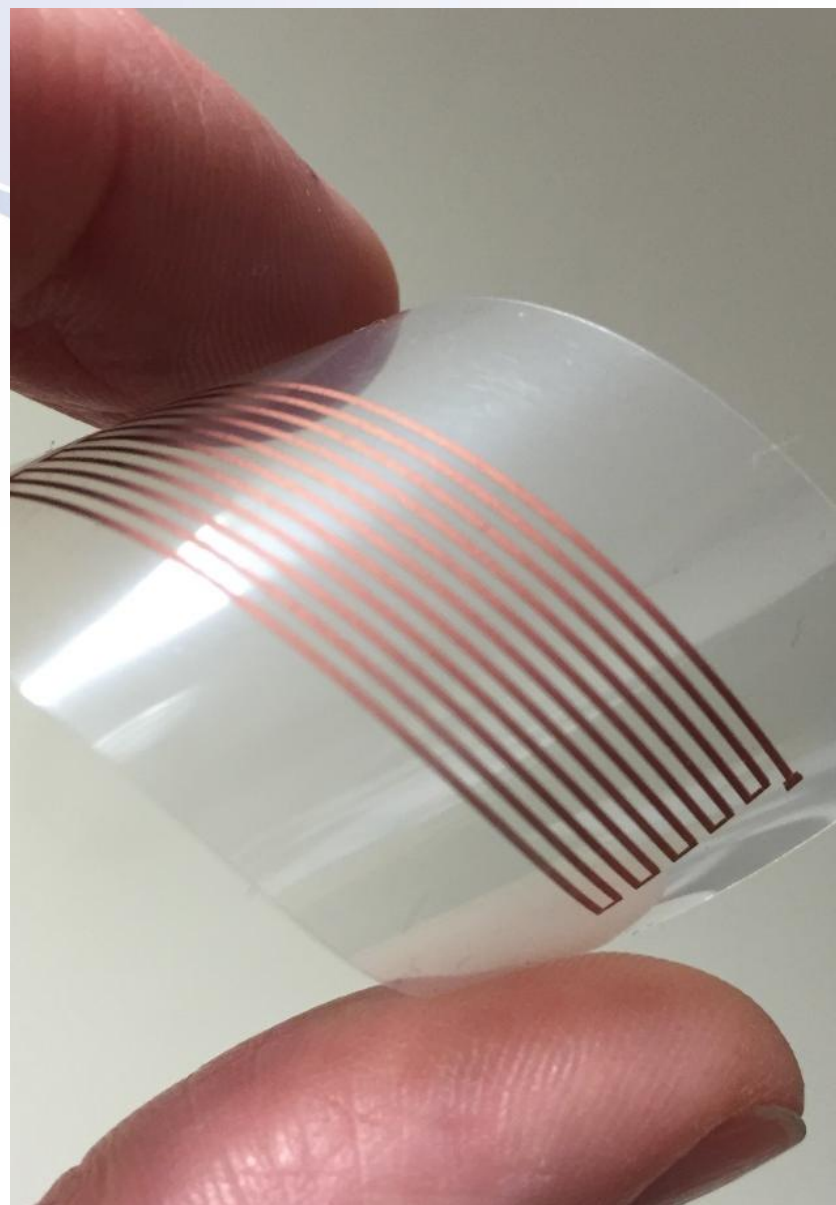


Hurdles (challenges?) to overcome

- Recessions
- Are nanomaterials toxic?
- What is a nanomaterial anyway?
- Nanomaterial registries
- REACH – hopefully this becomes an issue for us!

Conclusions

- CHS is an efficient and scalable route to the production of nanomaterial dispersions
- Promethean offer material manufacture as well as sales of custom built reactor systems.
- Production route offers significant advantages in terms of H&S compared to other routes to NMs
- Promethean's full scale reactor system has been commissioned and products are available in large volumes





PrometheanParticles



Formulating solutions with nanomaterials



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