Nanotechnology for Hydrogen production
A LCA study on photocatalytic hydrogen production with nanocarbon-inorganic hybrid material

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Objective

Hierarchically assemble functional nanomaterials into novel nanocarbon-inorganic hybrid structures for photocatalytic hydrogen production.
Nanocarbon –inorganic hybrids structures have been recently introduced as a new class of multifunctional composite materials.

The nanocarbon is coated by the inorganic material in the form of thin amorphous, polycrystalline, or single crystalline film.

The inorganic material is deposited from molecular precursor onto the surface.

The close proximity and similar size domain of the two phases (nonocarbon-inorganic) introduce the interface as a powerful new parameter.

Synergic interfacial processes such as charge and energy transfer resulted in structures with high potential as supercapacitors, fuel cells, photocatalytic application. Behind the interfacial effect the photocatalytic activity is also affected by the morphology and microstructure.

The scientific activities include the development of new functionalisation strategies targeted at improving charge transfer in hybrids and therefore their photocatalytic activity.
Objectivs

LCA analysis of photocatalytic H₂ production via the developed structures (Lab-scale and Pilot plant)

Comparison of photocatalytic H₂ production by the hybrid structures and the today’s mean for the hydrogen production
LCA analysis of photocatalytic Hydrogen production via hybrid structures – the LAB scale –
**Set-up study**

- **Functional unit**: Production of 1 kg hydrogen
- **Photoreactor**: 200 mL; \( H_2 \): 483 \( \mu \)mol/g h data based on experimental condition performed by INAEL
- **System boundaries**: From Cradle-to-gate
- **Established in SimaPro 8.1**, using ecoinvent data 3.1 (Alloc.Def)
- **Various data sources** (literature, personal communication, own calculations)
- **Impact assessment**: ReCiPe Midpoint

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**1. Starting materials**
- SWCNT production
- MWCNT production
- Graphene production
- CNT fiber production
- Cellulose production

**2. Chemical functionalisation**
- Sulfonitic oxidation
- Nitric acid oxidation
- Aromatic diazo couplings
- Isophtalic diazo couplings

**3. Hybridisation**
- Atomic layer deposition (Hybrid type 1)
- Wet-chemical deposition (Hybrid type 1)
- Electrospinning (Hybrid type 3)
- 3D Architectures (Hybrid type 2)

**4. Use (Hydrogen production)**
- Photoreactor (INAEL-Spain)
Environmental Impacts of the various production pathways for the hybrid structures

Production SWCNT

Production MWCNT

Production Graphene

Chemical functionalisation [1]

Hybrid, Type 1

Chemical functionalisation via Nitric acid oxidation

Hybrid, Type 2
(3D Architectures)

Production Photoreactor

Hybrid, Type 3
(Electrospun fibres)

Chemical functionalisation Sulfonitric oxidation

Results Lab-Scale

Environmental Impacts of the various production pathways for the hybrid structures
### Result Lab-Scale

**Chain 1.a:** MWCNT pathway  
**Chain 2:** CNT fiber pathway  
**Chain 3:** Cellulose Hydrogel pathway  
**Chain 4:** Graphene pathway
LCA analysis of photocatalytic Hydrogen production via hybrid structures

– the Pilot-plant scale –
Set-up Upscaling

- Assuming a daily production of 20 kg of hybrid material
- An ideal photoreactor (INAEL), lifetime 1700 h, 160 kg H₂
- The lab-scale data have been transformed/adapted based on the procedures in Piccinno et al., (2016), Gavankar et al., (2015), together with feedback from the project partners

Calculation assumptions from Lab-scale to Pilot plant- upscaling process:
- Input material (i.e. MWCNT): Linearly scaled up;
- Solvent: 63% less (recovery rate assumed);
- Electricity: 87% less;
- Emission: linearly scale-up;
Result

1) Photocatalytic Hydrogen production via oxidized and electrospun MWCNTs

- MWCNTs contribute to less than 0.3%.
- The functionalization shows low contribution to the overall impact – exceeding in all cases not 4% of the total.
- The hybridisation step contributes for most of the categories for 70 to 80% of the total impact;
- The Photoreactor shows only for one factor a value that is clearly above 30% (-> platinum catalyst).
2) Environmental impacts of the production of the photocatalytic (hybrid) material

- The final step (heating-crystallisation-chopping), the electrospinning, and the washing steps are the most dominant;
- The final step dominates – being responsible for more than 60% of the total impact (and going up to almost 85% for PMFP or TAP)
3) Environmental impacts of Heating-crystalization step

- Chemical input: argon, used as inert gas (consumption reduced by 62% in comparison to lab-scale) – but even this reduced argon consumption is responsible for up to 65% (TAP, PMFP) of impact of the hybrid material.

- Electricity consumption has been cut by 87% from the lab-scale to this upscaled scenario. Nevertheless, electricity consumption of this final step only is still responsible for more than 40% for all the impact categories.
Comparison of photocatalytic H$_2$ production by the developed material and today’s mean for its production
(Simplified) Life Cycle Assessment (LCA) study of various production pathways for the H\textsubscript{2} production

- **Functional unit**: Production of 1 kg hydrogen
- **System boundaries**

- Established in SimaPro 8.1, using ecoinvent data 3.1 ("cut-off" model)
- Various data sources (literature, personal communication, own calculations, …) used for the modelling of the different technologies;
- Mass allocation of the co-product (i.e. Pyrolysis: Diesel-Gasoline; NGSRM: steam)

**Technologies:**

- **Natural gas reforming** (also called “steam reforming”), the technology that largely dominates the current H\textsubscript{2} production (95% in the USA according to US DoE, 2015);
- **Biomass pyrolysis**, technology using renewable resources as starting point
- **High temperature electrolysis (HTE)** with solid oxide electrolysis cells (SOEC), a potential technology for large scale production in the long-term future
LCA analysis and comparison of today’s means of 1 kg hydrogen production

- Steam reforming of natural gas is set for each impact category as 100%.
- When comparing today’s technologies (i.e. steam reforming and pyrolysis) no clear conclusion could be drawn – then both technologies show the lowest values for some of the here examined environmental aspects (pyrolysis e.g. for GWP, ODP, TAP and FPD – steam reforming i.e. for PMFP, FETP).
- Future technology (i.e. HTE -Phot.) similar pattern with the exception for GWP FDP;
Conclusion and Remark

✓ A general overview of the environmental performance of hybrid structures:

The “best pathway “ for the production of Hybrid-nanocarbon materials has been identified.

The environmental impacts of photocatalytic H₂ production are mainly due to the Hybridization and Functionalization step (Energy and Chemical consumption-argon).

✓ A first baseline comparison with H₂ production technology.

The comparison shows that – when using the MWCNT – TiO₂ as photocatalytic material, the H₂ production is from an ecological point of view similar to HTE-(SOEC).

The impacts of photocatalytic H₂ production are governed by the high energy consumption (Hybrid material production) and by the low efficiency of the new developed material.

The comparison is affected by the difference in maturity of the compared technologies for the hydrogen production - and the differences in accuracy of the related inventory data- therefore our results need to be seen as an indicator for their respective (ecological) potential.
Conclusion and Remark

In our activities here, we have identified as the most critical issues:

- **LCI data availability** for novel types of materials (nanomaterials, specific chemicals, …)
- **LCIA of nano-related emissions** (e.g. in MWCNT synthesis) not included due to a lack of respective LCIA factors (especially in area of ecotoxicity and human toxicity);
- Need for more **reliable procedures** for the **upscaling** of new technologies!
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Environmental Impacts of the various production pathways for the hybrid structures

Chain 1.a and 1.d show the best environmental performance
SWCNT: For this project here, the producer of the material – the company Thomas Swan, one of the partners within the project – delivered respective material and energy flow data for the production process of this type of nanocarbon building blocks. However, due to confidentiality reasons, these inventory data can’t be displayed in details.

Environmental impact of 1 kg of Single-Wall Carbon Nanotubes (SWCNT)-Recipe Midpoint
Inventory data-Impact Assessment

MWCNT: Due to a lack of data from the producer, the production process for MWCNTs is modelled based on information found in public data sources (patents, scientific papers). MWCNT can be produced either by Laser Ablation or by Chemical Vapour Deposition (CVD). At Thomas Swan & Co Ltd. (TSwan) – the project partner producing these MWCNTs – the latter production method, i.e. CVD, is used. This process is the result of a close cooperation between the University of Cambridge and TSwan (Swan, 2005). For the modelling of the production of MWCNT, US Patent No. 8,173,211 B2 (Shaffer et al., 2012) assigned to the University of Cambridge (UK), has been used as the main source; assuming that this is the process that TSwan is using for its production. Then, further informations/details have been taken out by Healy et al., 2008, Kushnir and Sanden, 2008.

<table>
<thead>
<tr>
<th>INPUT</th>
<th>Amount</th>
<th>Unit</th>
<th>used ecoinvent dataset</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (Catalyst)</td>
<td>0.02</td>
<td>kg</td>
<td>silica fume, densified, market …, GLO</td>
<td>Split according to patent; Total amount catalyst from Healy et al. 2008 / nickel sulfate used as PROXY for nickel formate.</td>
</tr>
<tr>
<td>Ni formate Catalyst</td>
<td>3.4</td>
<td>kg</td>
<td>nickel sulfate, market for …, GLO</td>
<td></td>
</tr>
<tr>
<td>Argon (Carrier)</td>
<td>419</td>
<td>kg</td>
<td>argon liquid, market for …, GLO</td>
<td>According to patent 10x feedstock</td>
</tr>
<tr>
<td>Acetylene (Feedstock)</td>
<td>41.9</td>
<td>kg</td>
<td>acetylene, market for acetylene, GLO</td>
<td>Amount from Healy et al. 2008</td>
</tr>
<tr>
<td>Energy</td>
<td>1.4E+5</td>
<td>kWh</td>
<td>electricity</td>
<td>Amount from Healy et al., 2008 – split into electricity and heat according to Kushnir and Sanden, 2008</td>
</tr>
<tr>
<td></td>
<td>3.8E+5</td>
<td>MJ</td>
<td>heat, in chemical industry, steam production …, RER</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>OUTPUT</th>
<th>Amount</th>
<th>Unit</th>
<th>ecoinvent dataset</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>1</td>
<td>kg</td>
<td>carbon nanotubes, multi wall, MWCNT</td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td>419</td>
<td>kg</td>
<td>Argon, to air, urban air close to ground</td>
<td>Assumption: 100% of this is emitted to air</td>
</tr>
<tr>
<td>Acetylene</td>
<td>4</td>
<td>kg</td>
<td>NMVOC, non-methane volatile organic compounds, unspecified origin, to air, urban air close to ground</td>
<td>Assumption: 10% emitted to air / 90% recovered for further processing (cut-off)</td>
</tr>
<tr>
<td>Catalyst</td>
<td>-</td>
<td>-</td>
<td></td>
<td>NO end-of-life included</td>
</tr>
</tbody>
</table>
Environmental impact of 1 kg of Multi-Wall Carbon Nanotubes (MWCNT)-Recipe Midpoint
Graphene: In December 2014, Thomas Swan (UK) announced the start of its Graphene production on a kg/day basis via a liquid exfoliation process from graphite raw materials (Thomas Swann, 2014).

LCI data for this process have been established based on a publication in “Nature materials” from Paton and co-workers (Paton et al., 2014); publication that is describing a scalable production process by shear exfoliation in liquids.

**INPUT**

<table>
<thead>
<tr>
<th>Input</th>
<th>Amount</th>
<th>Unit</th>
<th>used ecoinvent dataset</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>1.43E+1</td>
<td>kg</td>
<td>Graphite, battery grade</td>
<td>-</td>
</tr>
<tr>
<td>NMP</td>
<td>3.77E+4</td>
<td>kg</td>
<td>N-methyl-2-pyrrolidone</td>
<td>Only “lost” amount taken into account here (remaining part remains within the system through distillation process)</td>
</tr>
<tr>
<td>Electricity</td>
<td>2.72E+6</td>
<td>kWh</td>
<td>Electricity, medium voltage (GB)</td>
<td>shear mixing &amp; centrifugation</td>
</tr>
<tr>
<td>Heat</td>
<td>1.67E+5</td>
<td>MJ</td>
<td>Heat, district or industrial, natural gas</td>
<td>distillation for NMP recovery</td>
</tr>
</tbody>
</table>

**OUTPUT**

<table>
<thead>
<tr>
<th>Output</th>
<th>Amount</th>
<th>Unit</th>
<th>ecoinvent dataset</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>1</td>
<td>kg</td>
<td></td>
<td>graphene, NMP exfoliation</td>
</tr>
<tr>
<td>solvent to HWI</td>
<td>3.77E+4</td>
<td>kg</td>
<td></td>
<td>Spent solvent mixture</td>
</tr>
<tr>
<td>graphite to HWI</td>
<td>1.33E+1</td>
<td>kg</td>
<td></td>
<td>Hazardous waste, for incineration</td>
</tr>
</tbody>
</table>

*Graphene:* A diagram showing the production process.

**INPUT**

- Graphite
- NMP
- Electricity
- Heat

**OUTPUT**

- Graphene
- solvent to HWI
- graphite to HWI

**Diagram Notes:**

- Graphite
- Solvent (*
- Solvent Recovery (Distillation process)
- Solvent, as WASTE
- Exfoliation (Shear mixing)
- Centrifugation
- Electricity
- Heat (Nat. gas)
- Graphene, as WASTE

**Graphene Production Process:**

1. Graphite is used as the primary input.
2. NMP is used as a solvent.
3. Electricity is used for processes like shear mixing and centrifugation.
4. Heat is used for distillation.
5. Graphene is produced as the output.
6. Solvent recovery and distillation are crucial steps for waste minimization.
CNT Fiber production

- Magnetic stirring and ultrasonication for 2 min (Electricity)

**Feedstock:**
- Butanol (97.7 wt%) + Ferrocene (0.8 wt%) + Thiophene (1.5 wt%)

1. CNT Precursors (Preparing the solution)
   - Pre-evaporator (Resistance)
   - Injection Pump

2. Furnace conditioning
   - Nitrogen stream for 10 min
   - Furnace heating slope 5°C/min from 20 to 1250°C
   - Extraction system
   - Vacuum pump (Vacuum pump (4 l/min)

3. Pre-Evaporation + Injection
   - Vacuum pump (4 l/min)
   - Injection Pump

4. Synthesis
   - Furnace at 1250°C
   - Rotation of the winders 60 rpm
   - Exchange gases valve:
     - Inlet stream (nitrogen)
     - Outlet stream (Vacuum)

5. Condensed CNT fibre
   - Densified with acetone
   - Heating at 350°C – 30 min

6. CNT fiber
   - Post treatment1
   - CNT fiber (condensed)
   - Evaporated Acetone

- Post treatment2
- Evaporated Acetone
- Pure CNT fiber (condensed)
- Pure CNT fiber (uncondensed)

**Final Materials**
## Goal and Scope

<table>
<thead>
<tr>
<th>System boundaries</th>
<th>Functional Unit</th>
<th>Energy and material input (manufacturing)</th>
<th>Energy and material input H₂ production</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOEC</td>
<td>Manufacturing SOEC and Hydrogen production</td>
<td>1 kg of H₂</td>
<td>Strazza, 2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Report: planSOECproject, 2010</td>
</tr>
<tr>
<td>NG-SRM</td>
<td>Hydrogen production</td>
<td>1 kg of H₂</td>
<td>Centinaya 2013</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>Biomass transport; Bio-oil production-upgrading;</td>
<td>1 kg of H₂</td>
<td>Zhang 2013 (from biomass transport to bio-oil production)</td>
</tr>
</tbody>
</table>
SOEC-H$_2$ production

Stack manufacturing: planar SOFC, 1 kW Sulzer Hexis, 0.2 Wcm$^{-1}$ (Karakassious, 2011)

Strazza, 2010 referred to 20 kWel tubular stack.

Water consumption: NREL 2004; Electricity consumption Barcero 2012 and SOEC-Plan report

3Nm3/h*8000h
Pyrolysis corn stover - Goal and scope

Data source: Zhang (2012)
F.U: 1kg H2