

# Life Cycle Energy and Climate Change Implication of Nanotechnologies: A Critical Review

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## <heading level 1> Summary

The potential environmental and health impacts of nano-technologies triggered a recent surge of life cycle assessment (LCA) studies on nano-technologies. Focusing on the energy use and greenhouse gas emissions impacts, we reviewed 22 LCA-based studies on nano-materials, coatings, photovoltaic devices, and fabrication technologies that were published until 2011. The reviewed LCA studies indicate that nano-materials have higher cradle-to-gate energy demand per functional unit, and thus higher global warming impact than their conventional counterparts. Depending on synthesis method, carbon-based nanoparticles, i.e., carbon nano-fibers, carbon nano-tubes and fullerenes require 1-900 giga joule per kilogram (GJ/kg) of primary energy to produce, compared with ~200 mega joule per kilogram (MJ/kg) for aluminum. This is mainly attributed to the fact that nano-materials involve an energy intensive synthesis process, or additional mechanical process to reduce particle size. Most reviewed studies ascertain, however, that the cradle-to-grave energy demand and global warming impact from nano-technologies in a device level is lower than from conventional technologies because nano-materials are typically used in a small amount to improve functionality and the upgraded functionality offers more energy efficient operation of the device. Due to immature status of most nano-technologies, the studies reviewed here often rely on inventory data estimated from literature values and parametric analyses based on laboratory or prototype production, warranting future analyses to confirm the current findings.

## <heading level 1> Introduction

Although various forms of nanotechnology-based products are phasing rapidly in to the areas of composite materials, solar cells, and energy storages, the environmental and health effects that nanotechnologies may pose are relatively unknown. A great deal of effort has been made to understand these effects in parallel with the progress of nanotechnologies by employing life-cycle assessment (LCA) that is widely regarded as a comprehensive tool for measuring a system's environmental impacts from cradle-to-grave; nano-sized material and waste flows can occur in any stages therein. Extremely rare inventory data, i.e. materials and energy inputs and emissions and waste outputs over the life cycle of nanoproducts and processes, have been the primary hurdle to such efforts, as most nanotechnologies are still immature or in Research and Development (R&D) status (Meyer et al. 2009; Khanna and Bakshi 2009).

Notwithstanding, there are pioneering LCA studies that utilize existing data or scientific modeling to estimate the potential- and real-environmental impacts. When detailed inventory data directly from industrial production are unavailable, such studies often adopt data from laboratory-scale or prototype production, and from literature on similar process products, or their own modeling; sometimes this information is extrapolated or adjusted to describe the nanotechnologies studied. Accordingly, the LCAs of nano-technologies inherently carry large uncertainties; careful and critical interpretation may be required when discussing their results. In addition, it is central to critically review existing LCAs and align their results based on key parameters to understand what might be expected in future when nanotechnologies become fully mature.

We reviewed 22 LCA based-studies on nanotechnologies published in journals and conference proceedings; here, we interpret their key results in a scientific context, and discuss their implications and limitations. The published LCAs are categorized into studies of nanostructured (single) materials, nanostructured composites, nanophotovoltaics, nanocoatings, and other technologies. Based on this classification, we discuss the energy-demand implication of nanotechnologies. We also compare inconsistent process assumptions and reporting methodologies across the studies and offer our interpretation of them. In conclusion, we summarize the key implications of the reviewed LCAs and suggest future directions. Our review will focus on the greenhouse-gas emissions and energy-related impacts and indicators, e.g., primary energy, as they are the most widely used ones in the reviewed studies and their evaluation methods are globally accepted, which allows us to compare impacts across technology types and maturity levels. Human health risk factors, another important aspect for public acceptance of any new technologies, were not included in this review.

### <heading level 1> Nanostructured single materials

Metal oxides or carbon nanoparticles are the most common nanomaterial studied by LCAs. Since these particles typically are used in small amounts to improve the function of a larger system, for example, as a filler of composite material, LCA studies normally consider only cradle-to-gate system boundary; the use and end-of-life stages are not examined. The first LCA study that investigated processes of (single) nanomaterial production was that on metal-oxide nanoparticles (titanium dioxide ( $\text{TiO}_2$ ) and zirconium dioxide ( $\text{ZrO}_2$ )) by Osterwalder and colleagues (2006). The processes of manufacturing  $\text{TiO}_2$  considered here include conventional sulfate- and chloride-processes, as well as flame synthesis from organic precursors. The large amount of organic precursors used in the latter process translated into 3-8 times higher carbon dioxide ( $\text{CO}_2$ ) emissions than the conventional sulfate- and chloride-based routes. The  $\text{CO}_2$

emissions per kilogram of  $ZrO_2$  via flame synthesis from precursors were considerably less than those of  $TiO_2$  (Table 1), mainly because  $ZrO_2$  has a higher molecular weight (123- versus 80-gram per mole), yielding more particles per volume. These authors also found that the plasma processes that subsequently vaporize and condense metals or oxides to produce nanoparticles generate the largest amount of  $CO_2/kg$  of  $ZrO_2$ . A  $TiO_2$  production route called the Altair Hydrochloride process later was explored by Grubb and Bakshi (2011) in terms of life-cycle impacts, fossil energy usage, and exergy. Their estimates of fossil energy requirement was higher than the previous one (Table 1) probably because their study is more comprehensive and inclusive considering the level of detail, besides the different process steps.

Khanna and colleagues (2008) investigated the life-cycle environmental impacts of vapor-grown carbon nanofibers (CNFs). In this synthesis, catalytic pyrolysis is used based on methane, ethylene, or benzene. Their analyses include in the system's boundary, the energy and materials inputs and outputs associated with reactor heating, the catalytic pyrolysis/CNF production, and separation and purification.

Khanna and colleagues found that the energy required for this process is extremely high, viz., 95-360 times higher than producing the same weight of steel depending on the feedstock, largely because vapor-phase manufacturing requires a high temperature (1000-1200°C) that is provided by electric heating (Khanna et al. 2008). In addition, low product yields, i.e., 50% for the methane- and ethylene-route, and 30% for that of benzene contribute a large degree to the high energy usage. Other environmental-impact profiles were consistent with these energy-intensity profiles. Since CNFs are not used independently, direct comparison with other metals may not be relevant. The same group later used this analysis in the LCA of CNF/plastic composite (Khanna and Bakshi 2009).

Carbon nanotubes have unique material properties suitable for many high tech applications, including hydrogen storage and in structural polymers. These nanostructured carbon tubes are parsed into single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) depending on the walls configuration. Healy and colleagues (2008) compared the life cycle environmental impacts of manufacturing single-walled carbon nanotubes (SWNTs) via three distinctive synthetic routes, namely, arc ablation (arc), chemical vapor deposition (CVD), and high-pressure carbon monoxide (HiPco). Their study attributes 99% of the environmental impacts to the electricity usage during synthesis and purification for all the three processes, ranging between 140-880 giga joule per kilogram (GJ/kg). For the base-case yield scenario, i.e., 4.50% for arc, 2.95% for CVD, and 0.08% for HiPco, the latter is the most environmentally benign manufacturing method because it uses the least amount of electricity for synthesis. The authors envision that, in a large-scale production, these inefficient laboratory-scale processes could improve dramatically, respectively yielding as much as 4, 7, and 600 times more than the current amount is feasible. This translates into large reductions in the environmental footprint per gram of SWNTs if it is scaled-up to commercial production lines.

The energy demand for producing carbon nanotubes was estimated in a separate study by Kushnir and Sandén (2008), modeling various carbon nanoparticles in scaled-up industrial conditions. According to their work, the production of SWNTs through the CVD process in fluidized bed reactors (FBRs) requires 2.4 GJ/kg of primary energy assuming a primary energy-to-electricity conversion factor of 0.3, much less than 880 GJ/kg estimated by Healy and colleagues (2008). This extensively lower estimate may, in part, be related to their assumption of higher carbon yield, i.e., 30% compared with 2.95% in the latter study. Moreover, the lower reactor temperature, 800°C used in FBR CVD compared with 1000°C in the Healy and colleagues study may be associated to the low process energy, 0.35 GJ/kg. In fact, the

majority (80%) of energy requirement in their study was attributed to producing materials, such as catalyst support, acids, and feedstock, in contrast to Healey's study wherein electricity usage for the CVD process dominates energy demand (99%). In the same study, Kushnir and Sandén (2008) estimated a scaled-up energy demand of producing SWNTs through the HiPco and electric-arc processes. Similarly, their primary energy estimates, 19 and 7.6 GJ/kg, were much lower than those reported by Healy and colleagues (2008). The authors also described the energy profiles of multi-walled nanotubes (MWNTs) production processes called Floating Catalyst CVD and Solar Furnace, which were found to be less energy-intensive than producing SWNTs (Table 1). Spherical nanoparticles called buckminsterfullerene or buckyballs (Iijima 1991) also identified as carbon 60 ( $C_{60}$ ) are commercially available and were modeled in this same study. The energy embedded in the feedstock, toluene, comprises 70% of the total primary energy demand of 8.8 GJ/kg as the process is inherently material intensive; only 5% of the carbon in feedstock is recovered, and 80% of the recovered carbon is in an unusable amorphous phase.

Ancil and colleagues (2011) studied the life cycle embodied energy of  $C_{60}$  and  $C_{70}$  fullerenes with a more inclusive scope of analysis encompassing synthesis, separation, purification, and functionalization with methyl ester groups. Four processing routes were investigated: pyrolysis with tetralin, pyrolysis with toluene, arc plasma and Radio Frequency (RF) plasma. According to their analysis, pyrolysis-based synthesis and separation processes are by far more efficient than plasma-based ones; the first and second processes, respectively use 12.7 and 17.0 GJ/kg, whereas the third and last processes, correspondingly require 88.6 and 106.9 GJ/kg. Their estimate of embodied energy for  $C_{60}$  from pyro-toluene process, i.e., 17 GJ/kg, is nearly twice as large as the one by Kushnir and Sandén (2008), i.e., 8.8 GJ/kg partly because of the more comprehensive system boundary used in their study. They found that purifying fullerenes to

electronic grade like in solar cell will double and triple the embodied energy of  $C_{60}$  and  $C_{70}$  respectively, due to a significant use of solvents, chemicals and electricity, underlining the variability of estimate depending on the size and purity. Functionalization of fullerenes further raises the embodied energy. According to their study, the cradle-to-gate of  $C_{60}$ -[6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) and  $C_{70}$ -PCBM, the fullerenes derivatives used as acceptor molecules in organic solar cells, including purification and functionalization require 64.7 and 90.2 GJ/kg, respectively, if the fullerenes are synthesized through pyro-tetralin route. The authors conclude that fullerenes are order of magnitude more energy intensive than other polymers; although fullerenes account for only 0.3 wt% of organic solar cells, they can comprise up to 19% of the total embodied energy. Although current organic solar cells suffer from high degradation rate in cell and packaging materials, they are known to potentially offer low energy industrial production due to the small amount of materials used for active layers. In a separate analysis, the authors estimate 0.3-0.8 years of energy payback time (EPBT) under a 1700 kilowatt-hour per square-meter per year ( $\text{kWh/m}^2/\text{yr}$ ) of solar irradiation for fullerene-based organic solar cells manufactured in laboratory conditions in comparison with 0.4-1.7 years for commercial inorganic solar cells (Anctil et al. 2010).

Kushnir and Sandén (2011) investigated the energy requirement from cradle to gate of nanomaterials lithium iron phosphate ( $\text{LiFePO}_4$ ) and lithium titanium oxide ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) used in cathode and anode of lithium (Li) batteries. The processes to fabricate these nanomaterials, hydrothermal and spray pyrolysis method, respectively, are more energy intensive (96 and 242 mega joule per kilogram (MJ/kg)) than the dry sintering used to produce the current reference materials for cathode ( $\sim 80$  MJ/kg). Moreover, the specific energy capacity of Li batteries based on these nanomaterials is lower than those based on the current cathode, lithium cobalt oxide ( $\text{LiCoO}_2$ ) and lithium cobalt nickel oxide ( $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$ ) and carbon anode. The authors estimated that the total energy demand per kWh capacity

of Li battery systems based on the former is 40-300% higher than the same based on the latter and carbon anode. However, the authors conclude that improved lifetime of nanomaterial based batteries will result in a net gain in terms of total life cycle energy efficiency if their lifetime stretches beyond 4000 deep cycles, compared with a range of 500-1400 deep cycles in the reference batteries.

Table 1: LCA Studies of Nano-structured (Single) Materials (the system boundary of these assessments is cradle-to-gate).

Reference	Material	Functional Unit	Data sources	Metrics	Results (Energy and GHG)
(Osterwalder et al. 2006)	TiO <sub>2</sub> ; ZrO <sub>2</sub>	1 kg	Literature; database	Energy; CO <sub>2</sub>	<u>Energy- TiO<sub>2</sub> (MJ/kg)</u> 32-40 (sulfate); ~19 (chloride) <u>CO<sub>2</sub> ó TiO<sub>2</sub> (kg CO<sub>2</sub>/kg)</u> 4-5 (hydrolysis); 15-30 (organic precursor) <u>CO<sub>2</sub> - ZrO<sub>2</sub> (kg CO<sub>2</sub>/kg)</u> 5 (hydrolysis); 9-20 (organic precursor); ~40 (plasma); ~35 (nano-milling)
(Grubb and Bakshi 2011)	TiO <sub>2</sub>	1 kg	Literature; patents; databases	Nonrenewable fossil fuel energy; exergy; Eco-Indicator 99 midpoint indicators <sup>1</sup>	<u>Energy (MJ/kg)</u> 116
(Khanna et al. 2008)	CNF	1 kg	Literature data for lab- scale production	Nonrenewable fossil fuel energy; CML midpoint indicators <sup>2</sup> ; Eco-Indicator 99 damage indicators (human health; ecosystem; resource)	<u>Energy with no recycling (GJ/kg)</u> 10.9 (from methane); 8.0 (from ethylene); 2.9 (from benzene)
(Healy et al. 2008)	SWNT	1 g	Process-based cost model; literature	Energy; carcinogens; airborne inorganics; climate change; acidification; land use; minerals	<u>Energy (electrical, GJ/kg)</u> 350 (arc); 880 (CVD); 140 (HiPco)
(Kushnir and Sanden 2008)	SWNT; MWNT; C <sub>60</sub>	1 kg	Technical reports; modeling	Energy	SWNT (GJ/kg) Arc- 7.6; FBR CVD-2.4; HiPco-19; laser ablation- 32 MWNT (GJ/kg) Floating catalyst CVD- 0.9; Arc-7.6; laser ablation-32; solar furnace- 0.8 C <sub>60</sub> (GJ/kg) Pyrolysis-9
(Sengul and Theis 2011)	CdSe QD	1 kg	Literature; modeling	Energy	70 GJ/kg

(Anctil et al. 2011)	C <sub>60</sub> ; C <sub>70</sub> ; PCBM	1 kg	Database; literature;	Energy	C <sub>60</sub> (Synthesis + separation, GJ/kg) Pyro Tetralin ó 12.7; Pyro Toluene ó 17.0; Plasma Arc - 88.6; Plasma RF ó 106.9 PCBM (GJ/kg) C <sub>60</sub> -PCBM - 64.7; C <sub>70</sub> -PCBM ó 90.2
(Kushnir and Sandén 2011)	LiFePO <sub>4</sub> ; Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>	1 kg	Modeling; literature	Energy	LiFePO <sub>4</sub> ó 96 MJ/kg Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> ó 242 MJ/kg

<sup>1</sup> carcinogens, respiratory organics, respiratory inorganics, climate change, radiation, ozone layer, ecotoxicity, acidification/eutrophication, land use, minerals, fossil fuels; <sup>2</sup> global warming potential, human toxicity potential, ozone layer depletion potential, photochemical oxidation potential, freshwater aquatic ecotoxicity potential, terrestrial ecotoxicity potential, acidification potential, eutrophication potential; TiO<sub>2</sub>= titanium dioxide; ZrO<sub>2</sub>=zirconium dioxide; CNF = carbon nanofiber; SWNT = single walled carbon nanotube; MWNT= multi walled carbon nanotube; C<sub>60</sub>=carbon 60; CdSe QD = cadmium selenide quantum dot; C<sub>70</sub>=carbon 70; PCBM = [6,6]-phenyl-C61-butyric acid methyl ester; LiFePO<sub>4</sub>= lithium iron phosphate; Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>= lithium titanium oxide; CML = Centrum Voor Milieuwetenschappen Leiden; GHG=greenhouse gas CVD=chemical vapor deposition; HiPco= high-pressure carbon monoxide; FBR=fluidized bed reactors; RF=radio frequency

## <heading level 1> Nanostructured Composites

Some LCAs are intended to estimate the environmental- and energy-benefits of replacing conventional materials with nanostructured composites. The benefits often are focused in the use phase of products, such as packaging film and automotive parts since most economic or environmental benefits are attained during this phase. The typical combination in nanostructured composites in the reviewed studies is that of using a polymer matrix with nanoparticle fillers. As summarized in Table 2, polypropylene (PP), low-density polyethylene (LDPE), and polyhydroxybutyrate (PHB) were used as the matrix with carbon nanofibers and nanoclay as fillers. These studies often utilized a comparative framework to highlight the environmental benefits of replacing conventional materials with nanocomposites. However, none describes commercial applications, relying instead for their analyses on published LCA databases and engineering modeling.

Lloyd and Lave (2003) examined the life-cycle environmental implications from the hypothetical case of substituting a steel-based automotive body panel with a clay-polypropylene (PP) nanocomposite. This change resulted in a mass reduction of 38-67% in the automotive body, as they derived from Young's modulus and the density of each material. Considering a U.S. hypothetical fleet of 210 million light-duty vehicles, this reduced mass, together with secondary mass-reductions in the chassis and power train based on equal driving performance, translated into reductions of 49-87 million metric tons of CO<sub>2</sub> emissions, and 5.7-10.1 billion gallons of gasoline usage. While this study offers a comprehensive mass-reduction model yielding fuel savings and thus environmental benefits during the use phase, the Economic Input-Output (EIO)-LCA framework they employed does not support detailed investigations into the production of the nanocomposite materials. Due to the aggregation of EIO-LCA databases that lack specific process data, the authors used the LCA data for the "Plastics Materials and Resins" industrial

sector as a proxy for the emissions, energies, and material flows in the life cycle of their nanocomposites. Accordingly, although the EIO-LCA based estimates may be a good approximation, the nanocomposites' environmental impacts were not fully distinguished from those of conventional materials. In contrast, the other studies reviewed here mostly use disaggregated and parameterized modeling to characterize nanotechnologies when detailed data are unavailable.

Roes and colleagues (2007) conducted a detailed process-based LCA of clay-polypropylene nanocomposite with data from a pilot plant. Comparing a clay/PP nanocomposite with a glass fiber /PP composite for an automotive internal panel, they reported negligible differences in the required weight (i.e., 20- versus 19.75 kg) and the life-cycle environmental impacts. For example, their estimates of life-cycle primary-energy demand (8.23- versus 8.21-GJ) and greenhouse gas (GHG) emissions (569- versus 570-kg CO<sub>2</sub>-eq.) of both composites are virtually identical. Notably, in this study, the clay/PP nanocomposite replaced a glass fiber/PP composite that is deemed conventional material, in an internal panel, whereas in Lloyd and Lave's study (2003) the nanocomposite was used in a body panel, replacing conventional metals.

In the same study, Roes and colleagues (2007) compared the life-cycle environmental impacts of this nanoclay/PP composite with conventional packaging and agricultural films that are made from polypropylene (PP) and low-density polyethylene (LDPE), respectively. Replacing the PP packaging film with the composite gave an estimated weight saving of 9%, but the savings were much higher, i.e. 36.5 %, when it replaced the polyethylene (PE) agricultural film. This higher saving stems from the significantly higher tensile-strength of the nanoclay/PP composite compared with the LDPE used in the conventional agricultural film.

The environmental impact of using nanoclay fillers to improve material properties was studied by Pietrini and colleagues (2007), wherein the authors compared the life-cycle energy and GHG emissions from applying nanoclay/biodegradable plastic composite to cathode ray tube (CRT) monitor housing and the automotive instrument panel. The biodegradable polymer matrix used in the composite, polyhydroxybutyrate (PHB), is less stiff than petroleum-based plastics. Therefore, the amounts of PHB nanocomposite used in the CRT monitor housing and the automotive instrument panel were estimated as being significantly higher than using conventional materials, i.e., 23-28% more than using high impact polystyrene (HIPS) for the CRT housing, and 32-36% more than using glass-fiber (GF)/polypropylene (PP) for the automotive panel. This translates into high energy and GHG emissions in applying nanoclay/PHB to the automotive internal panel where its increased weight raises fuel consumption during operation. On the other hand, as shown in Table 2, its usage as housing for the CRT monitor considerably lowered energy and GHG emissions depending on sources of PHB, viz., sugar cane (PHB1) or corn starch (PHB2).

The life-cycle energy implication of using carbon nanofibers (CNFs) in a polymer matrix composite was also described by Khanna and Bakshi (2009). Using the life-cycle energy of CNFs in Khanna and colleagues (2008), the authors concluded that producing polymer nanocomposites incorporating CNFs is 1.6-12 times more energy-intensive than producing steel with equal stiffness. Nevertheless, the scenarios of applying these composites to an automobile body panel resulted in net energy-savings except for some extremely conservative assumptions. The primary weight-savings of replacing a steel body panel with these composite materials ranged 18.9-61.2% depending on composite configuration; an additional 1 kg in reduction was assumed per kg of primary saving due to the related

changes in the automobile's design. For a body panel that constitutes 10% of the vehicle's weight, 3300 pounds (lbs.), the life-cycle energy savings from employing polypropylene matrix CNF composites was 18-65 GJ, excluding implausible recipes (9-15vol% CNF), with the high boundary corresponding to adding glass fiber. Using unsaturated polyester resin in place of polypropylene lowered the savings to 8-44 GJ/car.

Table 2: LCA Studies of Nanostructured Composites

Reference	Technology	Functional Unit	Data sources	Metrics	Results (Energy and GHG)	System boundary
(Lloyd and Lave 2003)	Nanoclay/PP	16.9 million light-duty vehicles; 210 million vehicles on the road	EIO-LCA database	Electricity; energy; conventional pollutants; GHG; fuels; ores; hazardous waste; toxic releases; water use	<u>lifetime savings for 16.9 million vehicles</u> Energy: 100-240 PJ; GHG: 7.2-16 million t CO <sub>2</sub> -eq. <u>annual fuel savings for 210 million light-duty vehicles:</u> gasoline: 5.7-10.1 billion gal CO <sub>2</sub> : 49-87 million t	Cradle-to-gate
(Roes et al. 2007)	Nanoclay/PP packaging film	1000 bags	Literature; Pilot-production data	NREU; climate change; abiotic depletion; ozone layer depletion; photochemical oxidant formation; acidification; eutrophication	<u>NREU (GJ/FU)</u> 0.284 (Nano) 0.283 (PP) <u>GWP (kg CO<sub>2</sub>-eq./FU)</u> 15.7 (nano) 15.9 (PP)	Cradle-to-grave
(Roes et al. 2007)	Nanoclay/PP agricultural film	coverage of 650 m <sup>3</sup>	Literature; Pilot-production data	Same as above	<u>NREU (GJ/FU)</u> 107.1 (Nano) 155.9 (LDPE) <u>GWP (kg CO<sub>2</sub>-eq./FU)</u> 5642 (nano) 9242 (LDPE)	Cradle-to-grave
(Roes et al. 2007)	Nanoclay/PP Automotive panel	Internal panel of low-weight family car over 150,000 km operation	Literature; Pilot-production data	Same as above	<u>NREU (GJ/FU)</u> 8.21 (nano); 8.23 (GF/PP) <u>GWP (kg CO<sub>2</sub>-eq./FU)</u> 570 (nano); 569 (GF/PP)	Cradle-to-grave
(Pietrini et al. 2007)	Nanoclay/PH B CRT monitor housing	17ö CRT monitor housing	Laboratory sample test data; literature; modeling	NREU, GWP	<u>NREU (MJ/FU)</u> 200.0 (HIPS); 8.9-22.9 (PHB1); 171.0-171.1(PHB2) <u>GWP (kg CO<sub>2</sub>-eq./FU)</u> 15.1 (HIPS); 10.5-1.3 (PHB1) ; 8.7-8.8 (PHB2)	Cradle-to-grave; Energy recovery
(Pietrini et al.	Nano-	Internal panel of	Laboratory	NREU, GWP	<u>NREU (GJ/FU)</u>	Cradle-to-

2007)	clay/PHB automotive internal panel	average car over 150,000 km operation	sample test data; literature; modeling		8.2 (GF/PP); 8.8-9.0 (PHB1); 10.3-10.6 (PHB2) GWP (kg CO <sub>2</sub> -eq./FU) 569.9 (GF/PP); 627.2-642.5 (PHB1); 700.6-722.8 (PHB2)	grave; Energy recovery
(Khanna and Bakshi 2009)	CNF/Polymer automotive body panel	Midsized car over 150,000 miles of operation.	Literature; PlasticsEurope; LCA databases; modeling	Energy	<u>Energy savings (GJ/FU)</u> 18 (CNF/PP); 65 (CNF-GF/PP); 8 (CNF-GF/UPR); 37-44 (CNF/UPR)	Cradle-to-gate; use

PP = polypropylene; PHB =polyhydroxybutyrate; CRT = cathode ray tube; EIO-LCA = Economic Input-Output LCA; GHG=greenhouse gas; NREU = nonrenewable energy use; GWP = global warming potential; FU = functional unit; HIPS= high impact polystyrene; GF=glass fiber; CNF=carbon nanofiber; UPR= unsaturated polyester resin

## <heading level 1> Nano-photovoltaics

Nanocrystalline dye-sensitized solar cells utilize a nanoparticle TiO<sub>2</sub> layer to host the charge-transfer dye in photovoltaic (PV) electricity generation (O'Regan and Gratzel 1991). An early LCA study by Greijer and colleagues (2001) compiled the life-cycle inventory of this type of PV, based on literature and hypothetical modeling. Since commercial production and operation data were unavailable, they developed scenarios combining the ranges of technical parameters, i.e., efficiency, lifetime, and production energy-demand in estimating prospective life-cycle impacts; this approach generated a wide range of CO<sub>2</sub> estimates, viz., 12-188 g CO<sub>2</sub>/kWh under solar irradiation of 2190 kWh/m<sup>2</sup>/yr. The lower bound corresponds to a lifetime of 30 years, an efficiency of 12%, and a process energy of 100 kWh/m<sup>2</sup>; the upper bound is based on a lifetime of 5 years, an efficiency of 7% , and a process energy of 280 kWh/m<sup>2</sup>. However, as efficiency may correlate with process energy, those estimates of upper- and lower-bounds are unlikely. Therefore, they further narrowed the estimates to 19-47 g CO<sub>2</sub>/kWh with 20-year lifetime. Veltkamp and de Wild-Scholten (2006) later investigated the EPBT and GHG emissions based on laboratory-scale production data for dye-sensitized cells (Veltkamp and de Wild-Scholten 2006). They also obtained a wide range of GHG estimates, i.e., 20-120 gram CO<sub>2</sub> equivalent per kWh (g CO<sub>2</sub>-eq/kWh) depending upon lifetime (Table 3).

Due to the exciting property offered by quantum dot photovoltaics (QDPVs), that is, Multiple Exciton Generation, researchers believe it could assure unprecedented efficiencies of over 40% in future (Klimov 2006), even though PV devices exploiting this phenomenon have not been manufactured.

engül and Theis (2011) estimated the potential environmental impacts of this technology using laboratory- production inventory data for cadmium selenide (CdSe) quantum dots (QDs). Their hypothetical PV is manufactured by a roll-to-roll deposition, typically used to produce thin-film

amorphous silicon (a-Si) PV modules. According to their assumptions, at 14% efficiency, 30-year lifetime, and 1700 kWh/m<sup>2</sup> of irradiation, this PV module (without Balance of System (BOS)) is responsible for only 5 g CO<sub>2</sub>-eq/kWh of GHG emissions and pays back the PV production energy in less than 1 year (Table 3). Although the energy demand to produce CdSe QD is extremely high, 70 GJ/kg (Table 1), due to the large amounts of solvents used to synthesize and purify the QD powder, its contribution to the overall energy profile is less than half the total as only small amount is needed for thin film QD PV.

Nanotechnology is also used to improve existing PV technology. Researchers found that the efficiency of amorphous silicon (a-Si) PV is significantly improved by hybridizing it with nanocrystalline-silicon (nc-Si) layers. We (Kim and Fthenakis, 2011) estimated the primary energy consumption and EPBT of hybrid a-Si/nc-Si PV designs by parametrically extrapolating the energy usage of current commercial lines based on a roll-to-roll deposition (Kim and Fthenakis 2011). Since the nc-Si layers must be thick (1000-3000 nanometer (nm)) to fully capture the target light spectrum compared to a-Si layer (200-300 nm), inserting nc-Si layers would considerably increase the electricity consumption and EPBT, without significantly increasing the module's efficiency. Accordingly, the EPBT of the current triple-junction a-Si module, 0.8 years, would rise to 0.9-1.1 years if its production is based on the current deposition rate. However, we suggested that if in future a module efficiency of 10% is achieved with a high-deposition rate of nc-Si (2.5 nanometer per second (nm/s)), the EPBT could drop to 0.5 years (Table 3). One such design called *δ*Micromorph<sup>o</sup>, an a-Si/nc-Si tandem cell already is commercially available from Oerlikon Solar. The life cycle greenhouse gas emissions of Micromorph were investigated by van der Meulen and Alsema (2011) based on a commercial process. They conclude Micromorph device requires 45% more energy to fabricate than the current a-Si module from the same manufacturer,

apparently associated with a thick additional nc-Si layer ranging 1300-2000 nm, much thicker than the 300-nm thick a-Si layer. In the batch process used for Micromorph, the reactor needs to be cleaned between layer depositions by injecting fluorinated gases of sulfur hexafluoride ( $\text{SF}_6$ ) or nitrogen trifluoride ( $\text{NF}_3$ ), potent global warming gases whose global warming potential is 22,800 and 17,200, respectively with a 100-year time horizon. Therefore, the life cycle GHG emissions of this device are closely associated to the type and usage of these Fluor gases, and fugitive emissions during the reactor cleaning and gas recycling/disposal stages. With scenarios of 0-10 wt.%  $\text{SF}_6$  release with recycling, the life cycle GHG emissions of Micromorph are 15-90% higher than the current a-Si device, while 0-3 wt.%  $\text{NF}_3$  release with thermal abatement scenarios result in 60-85% higher life cycle GHG estimates than the current a-Si design. The authors note that to offset these increased life cycle GHG emissions compared with a-Si, Micromorph needs to have an efficiency of 12-16% under the scenario of  $\text{NF}_3$  with thermal abatement. At the time of their study, the efficiency of Micromorph was 8-9% while a-Si had a 6.7% efficiency (van der Meulen and Alsema 2011).

Table 3: LCA Studies of Nano-structured PVs

Reference	Technology	Functional Unit	Data sources	Metrics	Parameters	Results (Energy and GHG)	System boundary
(Greijer et al. 2001)	nc-DSC	1 kWh	Literature; laboratory data	CO <sub>2</sub>	Irradiation= 2190 kWh/m <sup>2</sup> /yr Efficiency= 7, 9, and 12% Lifetime= 5-30 yrs Process energy= 100, 180, 220, and 280 kWh/m <sup>2</sup>	<u>GHG (system with 20 yr lifetime; g CO<sub>2</sub>/kWh)</u> Range: 12-188 19 (eff.= 7%; process energy=100 kWh/m <sup>2</sup> ) 22 (eff.=12%; process energy = 220 kWh/m <sup>2</sup> ) 25 (eff.=9%; process energy= 180 kWh/m <sup>2</sup> )	Cradle-to-grave
(Veltkamp and de Wild-Scholten 2006)	nc-DSC	1 kWh	Lab-scale industry data;	EPBT; GHG	Efficiency=8% Irradiation (kWh/m <sup>2</sup> /yr )=1000 (NW Europe); 1700 (S-Europe); 2190 (Sahara desert) Lifetime= 5-30 yrs PR= 0.75	<u>EPBT (system; yrs)</u> 1.3 (NW Europe); 0.8 (S-Europe); 0.6 (Sahara desert) <u>GHG (g CO<sub>2</sub>-eq./kWh)</u> 20-120 depending on lifetime	Cradle-to-gate; use
(Sengul and Theis 2011)	QDPV	1 kWh	Literature; database	EPBT; GWP; SOx; NOx; acidification potential; heavy metal emissions	Efficiency= 14% Lifetime=30 yrs	<u>EPBT (yrs)</u> 0.9 (module), 1.6 (system) <u>GHG (g CO<sub>2</sub>-eq/kWh)</u> 5 (module)	Cradle-to-gate; use; infrastructure
(Kim and Fthenakis 2011)	a-Si/nc-Si PV	1 m <sup>2</sup> of module	Industry; literature; database	Energy; EPBT	Irradiation= 1800 kWh/m <sup>2</sup> /yr Efficiency= 6.3% (aaa/aan/ann); 5.8% (an); 8% (future) PR= 0.75 deposition rate (nm/s)= 0.1-0.3 (a-Si, current); 0.2-0.4 (a-Si, future); 0.5-0.8 (nc-Si, current); 2-3 (nc-Si, future)	<u>Energy (module; MJ<sub>p</sub>/m<sup>2</sup>)</u> 860 (aaa); 750-1270 (an); 800-1390 (aan); 950-1510 (ann) <u>EPBT (module; yrs)</u> 0.8 (aaa-6.3%); 0.9 (an-5.8%); 0.9 (aan-6.3%); 0.7 (an-8%); 0.8 (aan-8%); 0.9 (ann-8%); ~0.5 (all, 10% with 2-3 nm/s deposition rate)	Cradle-to-gate; use
(van der	a-Si/nc-Si	1 m <sup>2</sup> of	Industry;	Energy;	Irradiation = 1700	<u>Energy (module; MJ<sub>p</sub>/m<sup>2</sup>)</u>	Cradle-to-

Meulen and Alsema 2011)	PV	module; 1 kWh	literature; database	GHG emissions	kWh/m <sup>2</sup> /yr, Efficiency = 6.7% (a-Si); 8.5% (a-Si/nc-Si), PR=0.75	1) Most likely -- 836 (a-Si, SF <sub>6</sub> ); 838 (a-Si, NF <sub>3</sub> ); 1219 (a-Si/nc-Si, SF <sub>6</sub> ); 1242 (a-Si/nc-Si, NF <sub>3</sub> ) 2) Oerlikon ó 719 (a-Si, SF <sub>6</sub> ); 720 (a-Si, NF <sub>3</sub> ); 1044 (a-Si/nc-Si, SF <sub>6</sub> ); 1069 (a-Si/nc-Si, NF <sub>3</sub> )	gate; use; capital equipment
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nc= nanocrystalline; DSC=dye-sensitized cell; QDPV = quantum dot photovoltaic; a-Si= amorphous silicon; nc-Si = nanocrystalline silicon; EPBT = energy payback time; GHG= greenhouse gas; GWP = global warming potential; SO<sub>x</sub>= sulfur dioxide; NO<sub>x</sub>=nitrogen oxide; PR = performance ratio; aaa= a-Si/a-SiGe/a-SiGe; an= a-Si/nc-Si; aan = a-Si/a-SiGe/nc-Si; ann = a-Si/nc-Si/nc-Si; SF<sub>6</sub>= sulfur hexafluoride; NF<sub>3</sub>=nitrogen trifluoride

## <heading level 1> Nano-coating

Nano surface coating improves materials properties and increases the durability of tools and equipment. Moign and colleagues (2010) compared the life-cycle impact of yttria-stabilized zirconia (YSZ) plasma-spray coating from a solution precursor that produces nanostructured coatings, with that of conventional suspension- and powder-plasma spray coatings. However, they found that the method of preparing the precursor does not make as much difference as the greatest impact (70-80%) comes from electricity usage during plasma-spray coating, which subsequently is related to the coating's duration and efficiency. However, Moign and colleagues (2010) did not report energy-consumption separately. In addition, the authors acknowledge that reliable data on properties and lifetime of the coatings from liquid plasma spray are not available, making it infeasible to compare the performance of YSZ nano-coatings with conventional ones.

On the other hand, when material utilization is extremely low, the impact of the material may be more important than process energy. Bauer and colleagues (2008) investigated the life-cycle environmental impact of titanium nitride (TiN), titanium aluminum nitride (TiAlN), and Ti + TiAlN coatings on a 6 millimeter (mm) diameter drill, using measured on-site data. They found that the production stage of the target metals, i.e. Ti, TiN, and TiAlN account for the largest share of environmental impacts, e.g., 75% of the global-warming potential. The study relates this finding to the low process-yield: coating efficiency is below 10%, and less than 50% of targets are consumed before they are exchanged.

In the same study, the authors investigated the potential life-cycle impacts by using carbon nanotube (CNT) coatings in field-emission-display (FED) technology (Bauer et al. 2008). They found

that the electricity consumption during the use phase accounts for the majority of primary-energy use (78.5%) and other environmental impacts (60-75%) from the FED screen's life cycle. Back glass accounts for 15-30% of those impacts, of which vapor deposition of the CNTs comprises 90% (Table 4). Accordingly, they estimated that the life-cycle impacts of the CNT-based FED screen are much less than those of liquid crystal display (LCD) - and cathode ray tube (CRT)-screens primarily because the former is assumed to use 50% less electricity than a similar LCD screen. Under this assumption, the GHG emissions generated over the life cycle of a FED screen are assessed as 25% of those from the life cycle of LCD screen.

Hassan (2010) explored the potential environmental benefits of coating concrete pavements with TiO<sub>2</sub> nanoparticles that are known to work as a photo-catalyst triggering chemical decomposition or oxidation of air pollutants such as nitrogen oxide, sulfur dioxide, and volatile organic compounds (VOCs) under ultraviolet light. The recipe of the surface-coating mixture was 2.3% TiO<sub>2</sub>, 22.3% cement, 66.8% filler, and 8.7% water. Although this mixture creates considerable emissions and energy demands from cradle to grave, for the amount of it used in a functional unit of 1 lane km with 5 mm thickness, the net environmental impact (-0.7) calculated by a Biological and Environmental Engineering (BEES)-impact assessment indicates that putting this mixture on concrete pavement is environmentally beneficial.

Table 4: LCA Studies of Nano-structured Coating

Reference	Technology	Functional Unit	Data sources	Metrics	Results (Energy and GHG)	System boundary
(Moign et al. 2010)	YSZ coating by SPPS, SPS, and APS	1 micrometer thick area of 1 m <sup>2</sup> surface	LCA Database; literature; patent; authors experience	EDIP single score impact	N/A	Cradle-to-gate
(Hassan 2010)	TiO <sub>2</sub> coating	Coating area of 1 lane km of pavement	EIO-LCA database; literature	BEES metrics <sup>1</sup>	<u>Energy (MJ/FU)</u> 1522.4 <u>GHG (t CO<sub>2</sub>-eq./FU)</u> 26.28	Cradle-to-gate; use
(Bauer et al. 2008)	PVD coating;	Coating of 100,000 drills with 6 mm diameter	On-site measurement; Databases	Energy; CML metrics <sup>2</sup>	<u>Energy (MWh/FU)</u> 27 (TiN); 40 (TiAlN); 59 (Ti + TiAlN)	Cradle-to-gate
(Bauer et al. 2008)	CNT coating	15ö-FED screen	Patent; personal communication	Energy; CML metrics <sup>2</sup>	<u>Energy breakdown (%)</u> use- 78.5; back glass coating-14.1; electronics-2.8; glass-1.2; front glass coating-0.5; housing-2.2; cable-0.4; disposal-0.4	Cradle-to-grave

<sup>1</sup> global warming, acidification, eutrophication, fossil fuel depletion, water intake, criteria air pollutants, human health (noncancerous), human health (cancerous), smog formation, ozone depletion, ecological toxicity; <sup>2</sup> aquatic ecotoxicity, ionizing radiation, photo-oxidant formation, ozone depletion, human toxicity, climate change, eutrophication, acidification, resource depletion; TiO<sub>2</sub>=titanium dioxide; PVD= physical vapor deposition; CNT= carbon nanotube; YSZ = yttria-stabilized zirconia; SPPS= solution precursor plasma spray; SPS = suspension plasma spray; APS=atmospheric plasma spray; FED = field emissions display; EIO-LCA= Economic Input-Output LCA; BEES =Biological and Environmental Engineering; CML= Centrum Voor Milieuwetenschappen Leiden; EDIP= Environmental Design of Industrial Products; FU= functional unit; TiN= titanium nitride; TiAlN= titanium aluminum nitride; N/A= not available

## <heading level 1> Nano-fabrication

There are LCA studies that deal with nanotechnologies that may not fall into the above classification because they involve nanofabrication processes that are difficult to specify because of the nature of systems studied. Krishnan and colleagues (2008) described the global warming and energy demand from manufacturing complementary metal-oxide-semiconductor (CMOS) microprocessors, including the impacts from chemical usage, silicon wafers, and semiconductor equipment (Table 5). By mapping the energy and process speed, the authors also observed increasing energy usages with decreasing process rates, consistent with our analyses (Kim and Fthenakis 2011) and those of Moign and colleagues (2010). On the other hand, Lloyd and colleagues (2005) calculated the potential energy-benefits of nanotechnologies in stabilizing platinum group metal (PGM) particles. They compared the expected changes of materials, energy inputs, and effluent outputs in meeting the expected emissions regulations by using current catalyst technology versus nanotechnologies that reduce the current PGM loading by 95%. Undoubtedly, the latter scenario entailed large savings of energy and emissions. However, the impacts related to realizing these nanotechnologies were not included, as the authors acknowledge, adding uncertainties to their conclusions.

Table 5: LCA Studies of Nanofabrication Technologies

Reference	Technology	Data sources	Functional Unit	Metrics	Results (Energy and GHG)	System boundary
(Lloyd et al. 2005)	Nanotechnology on Platinum-Group Metal Particles	EIO-LCA database; Gabi database	Projected motor vehicles in the US between 2005-2030	Energy; fuels; electricity; conventional pollutants; GHG; hazardous waste; toxic releases and transfers	Based on EIO-LCA data (Yr 2030): <u>energy change (TJ/FU)</u> +12700 (current), -22100 (nano) <u>GHG change (million kg CO<sub>2</sub>-eq./FU)</u> +1170 (current), -2030 (nano) Based on Gabi data (Yr 2030): <u>energy change (TJ/FU)</u> +13700 (current), -19300 (nano)	Cradle-to-gate; use
(Krishnan et al. 2008)	microprocessor	Industry; EIO-LCA database	1 wafer with 300-mm diameter	Energy; GHG	<u>Energy (GJ/FU)</u> 7.1 (device fabrication); 2.9 (silicon wafer); 2.5 (equipment); 1.51 (chemical); 14.1 (total production); 93-124 (use)	Gate-to-gate

EIO-LCA = Economic Input-Output LCA; FU = functional unit; GHG = greenhouse gas;

## <heading level 1> Discussion

The greatest challenge that most LCAs reviewed here faced is modeling the needed input- and output-flows of energy and material demands in the absence of information from commercial production lines. The LCAs of immature technologies described herein often offer only a snapshot of environmental impacts under R&D conditions. Even projected environmental impacts of future, mature technologies tend to encompass a large degree of uncertainty related to scaling factors. We classify in Table 6 the reviewed material studies according to their degree of commercialization and data sources. This may serve as a proxy to data quality, as the ideal LCAs should offer reproducible results describing stabilized manufacturing processes and product functions, typical of commercialized products. We note that a study of commercialized, mature products does not necessarily obtain data directly from industry. We identified only two studies, Bauer and colleagues (2008) and Krishnan and colleagues (2008) that have data from direct measurements representing industrial operations. Other studies rely on literature values, patents, laboratory- or pilot-data, or expertise in the area from which to formulate the key foreground materials and energy-input data in conjunction with scientific modeling. This again illustrates the difficulties in obtaining LCA data on nanotechnologies. The most nanocomposites in the reviewed studies of Lloyd and Lave (2003), Roes and colleagues (2007), and Khanna and Bakshi (2009) may represent mature technologies in terms of their material composition and properties, although their application scenarios reviewed here are not yet fully realized. Similar nano polymer composites are already used in automotive parts, for example, seat back sand consoles (Kang 2010).

In Table 6, we further classify the reviewed articles based on time perspective and production scale, which often related to the major performance and efficiency parameters such as nano-material process yield and PV conversion efficiency. Such categorization would provide additional comparability

across studies and help identify types of uncertainties and potential improvement in results. Commercial processes including pilot-scale operations tend to utilize energy and materials more efficiently than laboratory processes. On the other hand, the performance of a commercial product such as PV conversion efficiency often falls short of that realized in a laboratory condition. Comparing multiple studies for a system enables to identify the correlations between these parameters and time perspectives or production scales. For instance, different assumptions on process yield during the production of carbon nanotubes resulted in a large difference in energy estimates in the studies of Healy and colleagues (2008) and Kushnir and Sandén (2008). The former study adopted a laboratory-scale process yield, 4.5% and 2.95%, for synthesizing SWNTs through the Arc and CVD routes; the latter study assumed yields of 50% and 30% for the corresponding routes in their prospective analysis for large-scale production. This partially explains the more than an order-of-magnitude difference in the energy estimate between these two studies, 140-880 GJ versus 0.8-32 GJ per kg of SWNT. Also, the assumptions of industrial-level efficiency for chemical reactions may have contributed to the low energy demands of Kushnir and Sanden's study (Kushnir and Sanden 2008). In addition, laboratory-scale data often entails an extremely high usage of solvents for synthesis and purification of nanomaterials since the processes are not optimized for commercial production, as discussed in Engül and Theis (2011). This offers a large potential for improvement in LCAs in future when production is scaled up, and more data become available.

Table 6: Classification based on Technology/Process Maturity

Status	Study	System	Category	Time perspective /production scale
Commercial product available	(Osterwalder et al. 2006)	TiO <sub>2</sub> ; ZrO <sub>2</sub>	Material	Current-commercial
	(Grubb and Bakshi 2011)	TiO <sub>2</sub>	Material	Current-pilot
	(Khanna et al. 2008)	CNF	Material	Current-laboratory
	(Healy et al. 2008)	SWNT	Material	Current-laboratory
	(Kushnir and Sanden 2008)	SWNT; MWNT; C <sub>60</sub>	Material	Future-commercial
	(Hassan 2010)	TiO <sub>2</sub> coating on concrete pavement	Coating	Current
	(Moign et al. 2010)	YSZ coating	Coating	Current
	(Bauer et al. 2008)	PVD coating	Coating	Current-commercial
	(Krishnan et al. 2008)	Microprocessor	Fabrication	Current-commercial
	(Sengul and Theis 2011)	CdSe QD	Material	Current-laboratory
	(Anctil et al. 2011)	Fullerene	Material	Current
	(Kushnir and Sandén 2011)	LiFePO <sub>4</sub> ; Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>	Material	Current-commercial
	(van der Meulen and Alsema 2011)	a-Si/nc-Si PV	PV	Current-commercial; future
Under R&D for application	(Roes et al. 2007)	Nano-clay/PP to packaging/agricultural film, to automotive internal panel	Composite	Future
	(Greijer et al. 2001)	nc-DSC	PV	Hypothetical
	(Velkamp and de Wild-Scholten 2006)	nc-DSC	PV	Current-laboratory
	(Kim and Fthenakis 2011)	a-Si/nc-Si PV	PV	Current-laboratory; future
Early- or conceptual-stage	(Lloyd and Lave 2003)	Nano-clay/PP to automotive body panel	Composite	Hypothetical
	(Khanna and Bakshi 2009)	CNF/Polymer to automotive body panel	Composite	Hypothetical
	(Bauer et al. 2008)	CNT coating in FED screen	Coating	Hypothetical
	(Pietrini et al. 2007)	Nano-clay/PHB to CRT monitor	Composite	Hypothetical

		housing, to automotive internal panel		
	(Lloyd et al. 2005)	PGM particles in automotive catalyst	Fabrication	Future
	(Sengul and Theis 2011)	QDPV	PV	Hypothetical; laboratory

TiO<sub>2</sub>=titanium dioxide; ZrO<sub>2</sub>=zirconium dioxide; CNF=carbon nanofiber; SWNT= single-walled nanotube; MWNT= multi-walled nanotube; C<sub>60</sub>=carbon 60; YSZ=yttria-stabilized zirconia; PVD= physical vapor deposition; CdSe QD=cadmium selenide quantum dot; LiFePO<sub>4</sub>=lithium iron phosphate; Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>= lithium titanium oxide; a-Si= amorphous silicon; nc-Si = nanocrystalline silicon; PV=photovoltaic; PP=polypropylene; nc= nanocrystalline; DSC=dye-sensitized cell; CNT=carbon nanotube; FED=field-emission-display; PHB= polyhydroxybutyrate; CRT=cathode ray tube; PGM= platinum group metal; QDPV=quantum dot photovoltaic

In fact, many types of nanostructured single materials are commercially available (Kang 2010), including those listed in Table 6. The life-cycle environmental impacts of these materials were assessed more frequently than the other categories we describe here, perhaps because more inventory data are available. Their life-cycle energy demand tends to be higher than that of conventional micro structured counterparts of same materials because either extra energy is needed to mechanically reduce the particles size, or a gas-phase process requiring high energy-consumption is used for their synthesis (Osterwalder et al. 2006; Grubb and Bakshi 2011). For the carbon-based nanoparticles reviewed here, CNF, CNTs, and C<sub>60</sub>, their energy demand is exceptionally high, i.e., 1-900 GJ/kg (Table 1 and Figure 1) compared with widely used materials like steel, aluminum, and polymers whose production requires 30-220 MJ/kg (Khanna et al. 2008; Healy et al. 2008; Kushnir and Sanden 2008). However, comparing the impacts of nano-materials with those of conventional materials based on a produced mass or amount, e.g., 1 kg or 1 cubic meter (m<sup>3</sup>), could render a false conclusion without considering the performance of final products or the amount used for a defined function. The types of comparative analyses and their characteristics that applicable to LCAs of nanotechnologies are detailed in the study by Bauer and colleagues (2008).

The high energy intensities of nanomaterials including carbon-based-, metal oxide-, and quantum-dot nanomaterials, do not seem to trigger a high energy demand, at least based on the applications reviewed here. There are several reasons for this. First, nanomaterials comprise relatively small portion of a whole device or system as evident in most studies reviewed (Hassan 2010; Sengul and Theis 2011; Greijer et al. 2001; Veltkamp and de Wild-Scholten 2006; Khanna and Bakshi 2009; Bauer et al. 2008), so diluting their need for high energy-intensities. Figure 1 illustrates this tendency in energy intensities, wherein the high production-energy demand of carbon nanoparticles is not noticeable once they are used as fillers in CNF/polymer composites. In fact, all the composites evaluated need less energy to produce than do carbon nanoparticles. The production of biopolymer (PHB) based-composites especially has a small primary energy requirement, viz., less than 10 MJ/kg, due to the energy credits associated with growing biomass. There is an exception for this observation. Fullerenes used in organic solar cells account for as much as 19% of the total cell fabrication energy (Anctil et al. 2011). But, the overall energy demand to fabricate organic solar cells is expected to be smaller than other types of solar cells (Anctil et al. 2010). Second, from a life cycle perspective, the superior product performances of nanotechnologies offer considerable environmental benefits during the use phase that often exceed the high energy investment during the production stage, as described in Hassan (2010), Khanna and Bakshi (2009), Kushnir and Sandén (2011), and Sengül and Theis (2011). Importance of the use phase in accounting for life cycle impacts is also emphasized in other LCAs of PV and nanoclay/PP composites (Kim and Fthenakis 2011; Lloyd and Lave 2003; Roes et al. 2007; Pietrini et al. 2007).

We acknowledge that although well-accepted, the energy and climate change indicators that discussed in this review cannot fully capture the societal concerns of nanotechnologies; potential human health effects should be evaluated in parallel to understand the overall impacts and guide policies related to the risks of nanotechnologies. In fact, the potential health risks of exposure to nano-materials are not

well understood yet, thus not incorporated in LCA literature in general. Although some studies reviewed here include toxicities or human health metrics in their impact analysis (Khanna et al 2008; Hassan 2010; Bauer et al 2008), they are associated with upstream flows such as electricity generation.

## <heading level 1> Conclusions

Focusing on energy and greenhouse gas emissions matrix, we reviewed 22 LCA studies on nanotechnologies covering single materials, composites, PVs, coatings, and fabrication processes. Large variations were found across studies of major parameters, like process yields and efficiency, along with great diversity in the quality of the data. This undoubtedly is related to immature status of many nanotechnologies, which makes it difficult to obtain stable and reproducible information on energy, materials, and emissions data. We suggest that the high-energy demands to produce some nanostructured materials evaluated in previous LCA studies may not emerge as a primary concern. Often the energy demands of generating the nanomaterials are diluted over the life cycle as they are mixed with other substances to form composites, or as only small quantities are employed in surface coatings or in thin layers. The resulting improved efficiency in performance during the use phase, for example, increased fuel economy by replacing steel with nanocomposites, may even offer net energy benefits. However, we note that more LCA studies must be conducted to confirm this conclusion because the assessments we reviewed carry much uncertainty; often they rely on hypothetical scenarios and simplified parameters in the calculations due to dearth of data. As recently attempted for the energy-generation sectors (Farrell et al. 2006), harmonizing incongruous parameters, system boundaries, and reporting methodologies across LCA studies could somewhat reduce such ambiguities. In addition, to understand the overall benefits and costs of nanotechnologies, their risks to human health need to be included as another essential dimension.

Future update analyses are warranted to understand more completely the benefits and risks that nanotechnologies offer.

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Figure 1: Energy demand to produce nanostructured materials and composites in the reviewed studies.

CNF=carbon nanofiber; PP=polypropylene; TiO<sub>2</sub> = titanium dioxide; PHB= polyhydroxybutyrate; MJ/kg

= mega joule per kg