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Nano Insulation Materials: Synthesis and Life Cycle Assessment

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Abstract

The application of manufactured nanomaterials provides not only advantages resulting from their unique properties, but also disadvantages derived from the possible high energy use and CO_2 burden related to their manufacture, operation, and disposal. It is therefore important to evaluate the trade-offs of process economics with the associated environmental impacts in order to strengthen the existing advantages while counteracting disadvantages of nanomaterials. This is of particular importance at the early stage of the development, where different synthetic approaches with different energy and environmental impacts may be employed. We discuss here the importance of life cycle assessment (LCA) on the synthesis of nano insulation materials (NIMs) consisting of hollow silica nanospheres (HSNSs). The results indicate that the use of recyclable and environmentally friendly raw materials can improve greatly the process environmental footprints. New synthetic procedures are developed accordingly for HSNS NIMs with improved environmental features as well as thermal insulation performance.

1. Introduction

Environment, energy and sustainable development are being paid an ever increasing attention in the society of today. As buildings constitute a substantial part of the world's total energy use (~ 40%) and the greenhouse gas (GHG) emissions (~ 36% in the EU), improving the energy efficiency and reducing the GHG emission in the construction sector have without doubt been a crucial task [1]. One of the key strategies in this field is to increase the thermal insulation resistance of the building envelope in order to reduce the energy exchange through it [2-4]. The application of traditional thermal insulation materials, such as mineral wool, expanded polystyrene (EPS), extruded polystyrene (XPS), and polyurethane (PUR) foam to meet the energy efficient requirement have been suffering from the ever increasing thicker insulation thickness that is not desirable for many reasons, e.g., increased material consumption and cost, living space reduction, and architectural restrictions [2,3]. Moreover, the use of organic insulation materials such as EPS, XPS and PUR in buildings has limitations due to their safety issues, i.e., the release of toxic gases upon fire [2,3]. New and improved thermal insulation materials or solutions such as vacuum insulation panels (VIPs) and silica aerogels are under rapid development due to their extremely low thermal conductivity, 0.004–0.007 W/(m·K) for VIPs and 0.010–0.020 W/(m·K) for silica aerogels, respectively [5-7]. However, both VIPs and silica aerogels are costly solutions and their robustness for building applications may also be questionable [2,3]. It is obvious challenging to develop high performance and robust thermal insulation materials for building applications; not surprisingly, the research and development (R&D) of superinsulating materials, which usually refer to materials with a thermal conductivity below 0.025 W/(m·K) if air filled, below 0.020 W/(m·K) if gas filled, or below 0.015 W/(m·K) if evacuated, have attracted significant attention in the field [8].

We are interested in developing high performance thermal insulating materials by employing nanotechnology; conceptual nano insulation materials (NIMs) have been proposed and demonstrated with hollow silica nanospheres (HSNSs), where

a reduced thermal conductivity down to 0.020 W/(m·K) has been obtained [9-12]. Similar thermal conductivities have also been reported with hollow silica micro- and nanoparticles [13,14] and hollow polymer nanospheres [15]. The fact that solid and gas thermal conductions can be greatly suppressed at the nanometer scale indicates a promising pathway to achieve high performance thermal insulation materials by engineering their microstructures [10]. However, it must be pointed out that turning the conceptual NIMs into practical thermal insulation materials for building applications will require substantial R&D efforts dedicated to this field.

Nowadays, it is well accepted that any new materials or technologies shall be developed in accordance with the principles of sustainable development. Therefore, we suggest that the environmental feature of NIMs, such as embodied energy (EE) and carbon footprints (i.e. embodied carbon, EC), should be used as important parameters to guide the R&D, apart from their thermal insulation performance [11]. The application of NIMs or other manufactured nanomaterials provides not only advantages resulting from their unique properties that may shape the building industry, but also possible disadvantages derived from the high energy use and CO_2 burden related to their manufacture, operation, and disposal. Hence, it is important to evaluate the trade-offs of process economics with the associated environmental impacts in order to strengthen the existing advantages while counteracting disadvantages of NIMs or other nanomaterials [11]. However, compared to the great success on the synthesis and characterization of nanomaterials, only limited information is so far available for their environmental and energy features [16-18].

We report here a modified life cycle assessment (LCA) to evaluate the environmental impacts of HSNS NIMs and to optimize the corresponding material synthesis based on the LCA results. The motivation of this work is twofold. First, LCA is well known as a comprehensive framework that quantifies ecological and human health impacts of a product or system over its complete life cycle, which is obviously very interesting in the R&D of NIMs and other nanomaterials [11,18]. However, there are still many issues that need further precision for the application of LCA in the field of nanotechnology, e.g., the lack of necessary data/information for important raw materials or processes; consequently, a methodology that enables to overcome these difficulties is important and necessary. Second, the R&D of NIMs, similar to that for other nanomaterials or nanoenabled products, usually involve intensive trail syntheses in the early stage, where different synthetic procedures/strategies with different energy and environmental features can be employed [11]. A theoretical optimization of the involved synthetic procedures according to LCA is apparently important to lead the R&D of NIMs to the final product with improved environmental features as well as thermal insulation performance.

2. LCA inventory of HSNS NIMs

Fig. 1 shows the generic product system for HSNS NIMs. The following unit processes were considered within the LCA inventory analysis: synthesis of template, coating with SiO_2,

and the removal of template. The inputs/outputs for the product systems included raw materials, energy, water, final product, co-product, and emission to water and air. The end-of-life was not considered since it was not relevant to the synthesis of HSNS NIMs. Moreover, environmental burdens associated with recycling and human labor were excluded. Unit processes either producing the inputs (e.g. delivery of process energy and raw materials) or receiving the outputs (e.g. recycling of waste) were not included. It is worth noting that, in some circumstances, not every input/output can be modeled.
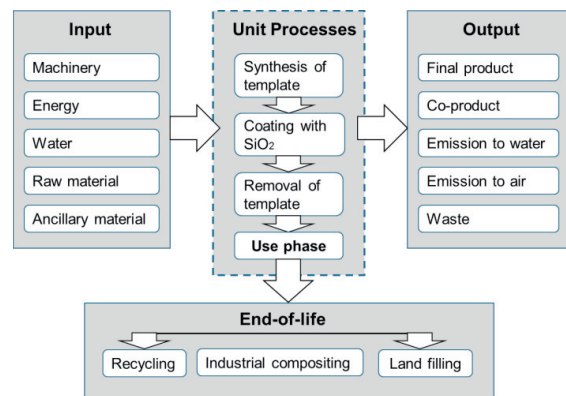

Fig. 1. Diagram for HSNS NIMs life cycle. Dotted lines indicate the boundary of the inventory analysis.

3. Synthesis and characterization of HSNS NIMs

In this work, a template-assisted wet chemical method was used to prepare HSNS NIMs [10,11], of which the involved three steps, i.e., synthesis of template nanospheres, coating them with SiO_2, and removal of the template were illustrated in Fig. 2. Monodisperse polystyrene (PS) nanospheres were selected as template for this study. For a typical synthesis, an aqueous solution of polyvinylpyrrolidone (PVP) and styrene was heated at 70°C; the polymerization reaction was initiated by adding potassium persulfate (KPS). To coat the obtained PS nanospheres, tetraethyl orthosilicate (TEOS) was used as the silica source and ethanol was used as reaction medium; the hydrolysis of TEOS was catalyzed by ammonium hydroxide (NH_4OH). Finally, the PS template nanospheres were burnt out at 500°C. During the synthesis, the material and energy consumption data were recorded and summarized in Table 1 and 2. About 1 g of HSNS NIMs with pore diameter of about 150 nm and shell thickness of 10–15 nm was obtained under the above mentioned synthetic conditions [10,11].
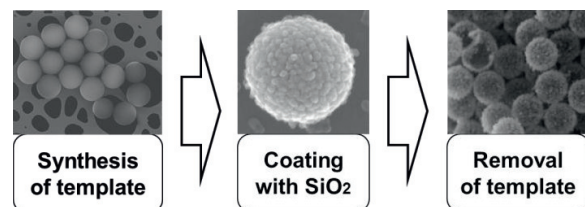

Fig. 2. Typical synthetic procedures for HSNS NIMs.

Table 1. Inputs for the synthesis of PS template nanospheres.

Material/Energy	Consumption	Supplier	Cost (EUR)[a]
Styrene	10 g	Sigma Aldrich	0.71
PVP	1.5 g	Sigma Aldrich	0.36
KPS	0.1 g	Sigma Aldrich	0.024
H_2O	110 g	In-house	0.011[b]
Electricity[c]	0.95 kWh	Trondheim Kraft	0.095

[a]: market price for raw materials may vary with suppliers and procurement policy. [b]: estimated as 0.1 EUR/kg, compared to that of tap water in Norway, 0.002 EUR/kg. [c]: 0.1 EUR/kWh.

Table 2. Inputs for the coating and removal of PS template nanospheres.

Material/Energy	Consumption	Supplier	Cost (EUR)
PS template	6 g	In-house	0.059[a]
Ethanol	162 g [b]	VWR	1.37
NH_4OH	3.6 g	Sigma Aldrich	0.26
TEOS	4.67 g	Sigma Aldrich	0.49
Electricity[c]	0.18 kWh	Trondheim Kraft	0.018
Electricity[d]	0.58 kWh	Trondheim Kraft	0.058

[a]: the synthesized PS nanosphere suspension. [b]: about 40 wt.% is used for cleaning purpose. [c]: for coating. [d]: for removal of PS template.

The as-synthesized materials were characterized by using scanning electron microscopy (SEM, Hitachi S5000). Thermal conductivity was measured with a Hotdisk Thermal Constants Analyzer (TPS 2500S). A disk-type Kapton Sensor 5464 with radius 3.189 mm was used. The sensor, which acts both as heat source and temperature recorder, was sandwiched in two parts of powdered samples. The temperature increase of the samples as a function of time was recorded to compute the thermal conductivity (uncertainty: ~ 5%). The final thermal conductivity value reported here was the arithmetic mean of four individual measurements under different conditions (heating power: 0.02–0.20 W; measurement time: 1–160 s).

4. Results and discussion

4.1. Structural features of HSNS NIMs

A hollow or porous structure that takes the advantage of air cavities with low thermal conductivity (about 0.026 W/(m·K) at standard temperature and pressure condition) is important for thermal insulation. For superinsulating materials with thermal conductivities lower than that of normal air, nanoporous materials/structures are usually considered, taking the advantages of size-dependent thermal conductivity of both the gas and the solid phase [10,11]. In this work, HSNS NIMs are in fact an aggregation of HSNSs, as shown in Fig. 3. It is obvious that the overall property of HSNS NIMs will depend on several parameters, such as the dimension (diameter and shell thickness) of the HSNSs, the type of the filled gas, and the packing manner of the HSNSs, Fig. 4. Since the solid thermal conductivity for a nanosphere aggregation is usually small due to the existence of a "neck area" (contact area) with typical sizes of a few nanometers between adjacent nanospheres [19], reducing the contributions from the gaseous phases, i.e., the isolated air cavities that are trapped inside the HSNSs and the interconnected air cavities between the HSNS NIMs, are important to achieve HSNS NIMs with low thermal conductivities.
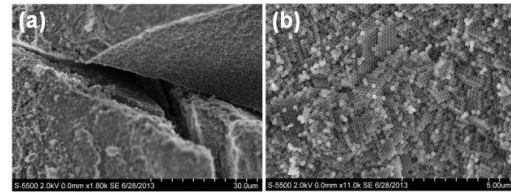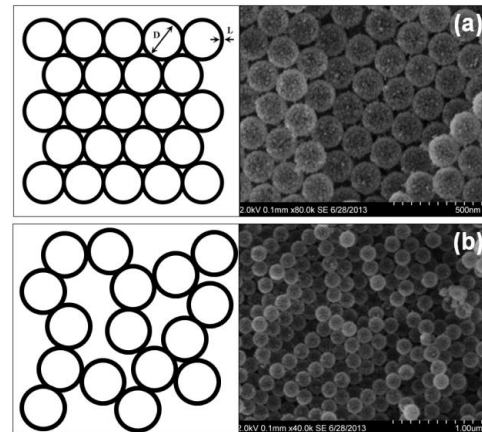

Fig. 3. SEM images of HSNS NIMs.

Fig. 4. Hexagonal close packing (a) and random packing (b) of HSNS NIMs.

An effective thermal conductivity of about 0.02 W/(m·K) can be achieved with HSNS NIMs with pore diameter of about 150 nm and shell thickness of 10–15 nm [10,11,14]. The effective thermal conductivity varies with measurement conditions, implying that the packing manners (Fig. 4) should also be taken into account when analyzing the thermal performance of HSNS NIMs. Moreover, recent studies on HSNS NIMs show that reducing the shell thickness has a larger effect on the measured thermal conductivity compared to reducing the pore diameters. This indicates that the isolated air cavities trapped inside the HSNSs are less important to the overall performance of the structure. For example, similar thermal conductivities have been observed for HSNS NIMs with similar shell thickness but different pore diameters of ~ 200 nm and ~ 400 nm. It suggests that HSNS NIMs might be prepared with larger PS template nanospheres, which is consistent with the findings reported by Yu et al. [13].

4.2. Process economics of HSNS NIMs

A cost analysis on HSNS NIMs was performed to evaluate the process economics at a laboratory scale. However, it must be noticed that some figures may vary significantly when upscaling the synthesis to an industrial level. As shown in Fig. 5a and 5b, the energy (i.e. electricity) consumption is in general small, 3–8%, when compared to those of the raw materials. For the synthesis of PS nanospheres, there is a significant contribution, about 30%, from the use of PVP, which is an additive to control the size of PS nanospheres. Larger PS nanospheres would be obtained at smaller dosage of PVP [12]. For the coating process, the use of ethanol

constitutes a substantial part of the total cost, which is very similar to those observed for the environmental features of HSNS NIMs [11] and silica aerogels [20], indicating also that ethanol needs to be used more efficiently to improve the process economics.
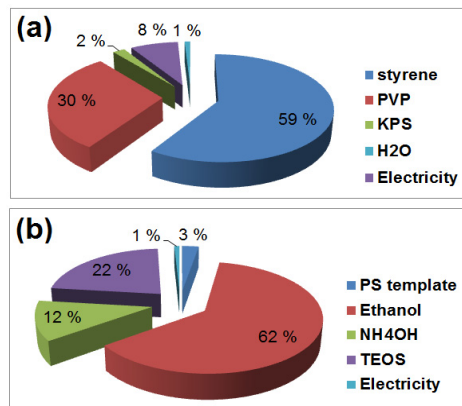

Fig. 5. Cost analysis of (a) the synthesis and (b) the SiO_2 coating of PS nanospheres.

It is worthwhile to note that only limited information is available for the energy and environmental features of the employed raw materials [11], implying that a certain degree of simplification has to be performed in this work. As shown in Fig. 3 and 4, HSNS NIMs are actually made of silica and air, where the silica is from TEOS–the silica source material used in this work; the other materials, e.g. PS templates and ethanol, are supplementary inputs for the growth of HSNS NIMs at certain conditions. In this regard, the EE and EC of HSNS NIMs can be expressed as: $EE_{HSNS-NIMs} = EE_{TEOS} + EE_{process}$ and $EC_{HSNS-NIMs} = EC_{TEOS} + EC_{process}$. Unfortunately, the embodied energy and carbon data for TEOS, though important to evaluate the environmental impact of HSNS NIMs, are not available so far [11,20]. However, it is necessary to evaluate the contribution from the synthetic processes in order to optimize the synthesis of HSNS NIMs to improve their environmental impacts. As reported in Table 3, HSNS NIMs have a significant high environmental impact in the operational phase, i.e., $EE_{process} = 2.685$ MJ/g and $EC_{process} = 8.4$ g CO_2/g, which is not very surprising since the analysis is based on a small amount of material. For example, in a previous study, Dowson et al. reported also a high EE value of ~ 7.3 MJ/g for silica aerogels made by supercritical drying [20].

Table 3. Embodied energy and carbon of the operational phase.

Material/Energy	Amount	$EE_{process}$ (MJ/g)	$EC_{process}$ (g CO_2/g)
PS nanosphere	0.5 g [a]	0.054	1.7
Ethanol	162 g	2.543	1.8
NH_4OH	1.05 g [b]	0.045	2.5
Electricity[c]	0.81 kWh	0.043	2.4
Sum		2.685	8.4

[a]: the amount of PS nanospheres. [b]: the amount of NH_3 in NH_4OH solution (28-30 wt.%). [c]: see Appendix for detailed calculation.

A LCA data interpretation has been performed to shed light on the environmental features of HSNS NIMs. First, it is found that the use of ethanol is an obvious drawback for the current synthesis. As shown in Table 3, the use of ethanol represents the most energy intensive step in the whole process; whereas the environmental effect is found to be more significant with NH_4OH, which acts as a catalyst during the hydrolysis of TEOS. These findings are useful to design new synthetic routes, where the use of ethanol and NH_4OH may be reduced or replaced with other materials.

It is also worthwhile to note that a large scale synthesis, where the raw materials and electricity can be used more efficiently, is important to reduce the process economics of HSNS NIMs. For example, the present experimental conditions (Table 2) can be readily adapted (*e.g.,* by increasing the amount of PS template and TEOS) to the synthesis of ~ 2 g HSNS NIMs, where reduced embodied energy and carbon values of about 1.37 MJ/g and 5.4 g CO_2/g, can be obtained (see Fig. 6). However, the reduction of the EE and EC in the operational phase of HSNS NIMs does not linearly follow the upscaling of the synthesis. For example, the EC from PS template nanospheres becomes increasingly important to that of the final product, which is due to the fact that, as a sacrificed template, the PS nanospheres need to be removed to obtain the final product. However, PS has a high embodied energy, about 109 MJ/kg (see Appendix); then the EE as well as EC of the PS template nanospheres will be transferred to those of HSNS NIMs if the PS template nanospheres cannot be recycled/reused properly. In this regard, PS nanospheres are not a good template material for the synthesis of HSNS NIMs with reduced environmental impacts.
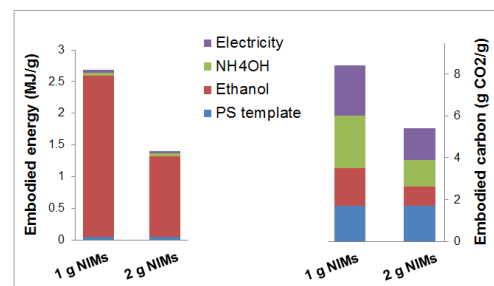

Fig. 6. Environmental features of HSNS NIMs at different conditions.

4.3. Optimization for the synthesis of HSNS NIMs

Based on the above LCA discussion, the synthetic procedure of HSNS NIMs can be optimized. For example, the reaction medium, ethanol, can be replaced with water if sodium silicate (i.e. water glass) is selected as silica source [21]. Replacing ethanol with water would dramatically change the process economics as shown in Fig. 5 and 6. Moreover, the use of water glass instead of TEOS has indeed been used in aerogel industry to reduce the manufacture cost and environmental feature of aerogel materials. A recent trail synthesis in aqueous medium indicates that the hydrolysis of sodium silicate under acidic environment results in the

formation of SiO_2, which can be easily captured by the preexisted PS template nanospheres [21], as shown in Fig. 7. Thermal conductivity measurements and other details will be reported later. It is also necessary to replace PS template nanospheres with other environmental friendly materials. $CaCO_3$ nanoparticles have been tried with such purpose, though the coating process with either TEOS or sodium silicate remains difficult at this stage.
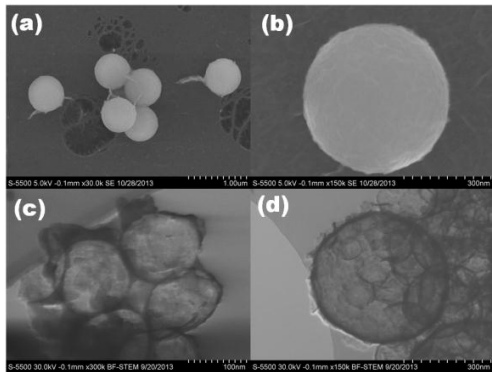

Fig. 7. SiO_2 coated PS nanospheres (a and b) and HSNSs after removal of PS templates (c and d). A water glass based synthesis is used [21].

5. Conclusions

HSNS NIMs exhibit a reduced thermal conductivity of down to 0.02 W/(m·K) due to the predominant size-dependent thermal conduction appearing at nanometer scale. The cost and energy and raw material consumption related to the synthesis of HSNS NIMs have been analyzed according to life cycle assessment (LCA). It is found that HSNS NIMs exhibit a relatively high environmental impact. The LCA results indicate also that the efficient use of raw materials, upscaling production, and the use of environmentally friendly materials can affect greatly the process economics of HSNS NIMs. New synthetic approaches can thus be developed to optimize their environmental impacts. Further studies dedicated to HSNS NIMs with low thermal conductivities and low environmental impacts are interesting and worth pursuing.

Acknowledgements

Appendix A. Embodied energy and carbon data

In literature the embodied energy and carbon data (i.e. EE and EC) of the raw materials used in this work are available, e.g., from Ecoinvent database Version 3, though values are usually varied with different boundary conditions.

Polystyrene (PS) usually has a high EE and EC, ranging from 86 to 109 MJ/kg and 2.7 to 3.4 $kgCO_2$/kg, respectively [22,23]. In this work, higher values are used to represent PS template nanospheres with a possible high environmental impact. The EE and EC of ethanol vary with the production method [24]. Detailed EE and EC data used for the calculation of process economics are listed in Table A.

Table A. Inventory for embodied energy and carbon.

Material	EE (MJ/kg)	EC ($kgCO_2$/kg)	Reference
PS	109	3.4	22,23
Ethanol	15.7	0.0115	23,24
NH_3	43.15	2.41	23,25
Electricity (/kWh)	0.0525	0.003	25,26

References

[1] Marszal AJ, Heiselberg P, Bourrelle JS, Musall E, Voss K, Sartori I, Napolitano, A. Zero Energy Building–A review of definitions and calculation methodologies. Energ Buildings 2011;43:971-979.

[2] Jelle BP, Gustavsen A, Baetens R. The path to the high performance thermal building insulation materials and solutions of tomorrow. J Build Phys 2010;34:99-123.

[3] Jelle BP. Traditional, state-of-the-art and future thermal building insulation materials and solutions–Properties, requirements and possibilities. Energ Buildings 2011;43:2549-2563.

[4] Papadopoulos AM. State of the art in thermal insulation materials and aims for future developments. Energ Buildings 2005;37:77-86.

[5] Baetens R, Jelle BP, Thue JV, Tenpierik MJ, Grynning S, Uvsløkk S, Gustavsen A. Vacuum insulation panels for building applications: A review and beyond. Energ Buildings 2010;42:147-172.

[6] Simmler H, Brunner S. Vacuum insulation panels for building application. Energ Buildings 2005;37:1122-1131.

[7] Baetens R, Jelle BP, Gustavsen A. Aerogel insulation for building applications: A state-of-the-art review. Energ Buildings 2011;43:761-769.

[8] www.inive.org. Superinsulating materials 2012.

[9] Jelle BP, Tilset BJ, Jahren S, Gao T, Gustavsen A. Vacuum and nanotechnologies for the thermal insulation materials of beyond tomorrow–From concept to experimental investigations. *Proceedings of the 10th International Vacuum Insulation Symposium (IVIS X)*, Ottawa, Canada, 2011;171–178.

[10] Gao T, Sandborg LIC, Jelle BP, Gustavsen A. Nano insulation materials for energy efficient buildings: A case study on hallow silica naonspheres, in Mendez-Vilas A. *Fuelling the Future: Advances in Science and Technologies for Energy Generation Transmission and Storage.* Boca Raton:BrownWalker Press; 2012;535-539.

[11] Gao T, Jelle BP, Sandborg LIC, Gustavsen A. Monodisperse hollow silica nanospheres for nano insulation materials: Synthesis, characterization, and life cycle assessment. ACS Appl Mater Interfaces 2013;5:761-767.

[12] Sandberg LIC, Gao T, Jelle BP, Gustavsen A. Synthesis of hollow silica nanospheres by sacrificial polystyrene templates for thermal insulation applications. Adv Mater Sci Eng 2013;483651.

[13] Yue Q, Li YZ, Kong M, Huang JC, Zhao XJ, Liu J, Williford RE. Ultralow density, hollow silica foams produced through interfacial reaction and their exceptional properties for environmental and energy applications. J Mater Chem 2011;21:12041-12046.

[14] Liao Y, Wu XF, Liu HD, Chen YF. Thermal conductivity of powder silica hollow spheres. Thermochim Acta 2011;526:178-184.

[15] Luo Y, Ye C. Using nanocapsules as building blocks to fabricate organic polymer nanofoam with ultra low thermal conductivity and high mechanical strength. Polymer 2012;53:5699-5705.

[16] Handy RD, Owen R, Valsami-Jones E. The ecotoxicology of nanoparticles and nanomaterials: current status, knowledge gaps, challenges, and future needs. Ecotoxicology 2008;17:315-325.

[17] Batley GE, Kirby JK, McLaughlin MJ. Fate and risks of nanomaterials in aquatic and terrestrial environments. Acc Chem Res 2013;46:854-862.

[18] Hischier R, Walser T. Life cycle assessment of engineered nanomaterials: State of the art and strategies to overcome existing gaps. Sci Total Environ 2012;425:271-282.

[19] Desai TG. Thermal transport in nanoclusters. Appl Phys Lett 2011;98:193107.

[20] Dowson M, Grogan M, Birks T, Harrison D, Craig S. Streamlined life cycle assessment of transparent silica aerogel made by supercritical drying. Appl Energ 2012;97:396-404.

[21] Sandberg LIC. Unpublished results.

[22] Hannond GP, Jones CI. Inventory of carbon and energy (ICE). Version 1.6a, Department of Mechanical Engineering, University of Bath, 2008.

See www.bath.ac.uk/mech-eng/sert/embodied/ for futher details. Accessed 01/11/2013.

[23] www.ecoinvent.ch

[24] Lorenz D, Morris D. How much energy does it take to make a gallon of ethanol? Institute for Local Self-Reliance (ILSR), 1995.

[25] Bhat MG, English BC, Turhollow AF, Nyangito HO. Energy in synthetic fertilizers and pesticides: Revisited. Oak Ridge National Laboratory, 1994, ORNL/Sub/90-99732/2.

[26] www.ipcc.ch/pdf/special-reports/sroc/Tables/t0305.pdf