

Simple Metal-catalyst-free Production of Carbon Nanostructures

Thomas K. Ellis,^A Christian Paras,^B Matthew R. Hill,^B
and John A. Stride^{A,C,D}

^ASchool of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia.

^BCSIRO Division of Materials Science and Engineering, Private Bag 33,
Clayton South MDC, Vic. 3169, Australia.

^CBragg Institute, Australian Nuclear Science and Technology Organisation,
PMB 1, Menai, NSW 2234, Australia.

^DCorresponding author. Email: j.stride@unsw.edu.au

We report the metal-catalyst-free production of multiwalled carbon nanotubes and nanobubbles, in a chemical reduction of hexachlorobenzene by metallic sodium, giving high yields (in excess of 80 %) and at temperatures as low as 190°C for multiwalled carbon nanotubes and 100°C for nanobubble formation. The carbon nanotube samples produced under solvothermal conditions were found to consist of large bundles of nanotubes (>50 μm) consistent with a facial growth from the surface of the molten metal. Meanwhile, the nanobubbles produced under ambient pressure were found to be small ($\leq 1 \mu\text{m}$), polydispersed (smallest $\sim 50 \text{ nm}$), and the bulk to have a large microporous area. With the regulatory complexities and high environmental and economic costs of remediating waste containing highly hazardous halogenated aromatic chemicals, necessitating high-temperature incineration under strictly controlled conditions, this low-temperature, low-cost chemical degradation of hexachlorobenzene is of great potential as a scalable and workable remediation technology.

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Introduction

The decades that have followed on from the remarkable discoveries that elemental carbon has allotropes that exist as discrete nanometre-scale structures, from zero-dimensional sub-nanometre closed-shell fullerenes^[1] through to high-aspect-ratio (α) carbon nanotubes (CNT), approximately 1 nm in width and now up to a millimetre in length ($\alpha > 10^6$),^[2] have coincided with the recognition of the field of nanotechnology as a distinct research discipline in which experimental and material frontiers can be crossed. A central tenet in much of this research effort has been the drive to simplify the synthetic pathways to many of the nanostructures that are now known, making large-scale production economically viable and ultimately leading to the commercialisation of these highly novel materials. The initial production methods of nanostructured carbons such as fullerenes and CNT were based around vacuum-chamber techniques including arc discharge,^[3,4] laser ablation,^[5] and chemical vapour deposition reactions.^[6] Although these are known to facilitate precise control of the nanostructure morphology and size, which have led to well-defined arrays and patterning of CNT on surfaces, they all have the common problem of being expensive to scale up, thereby restricting the materials to the research laboratory, or high-value applications. Another drawback of these approaches in making CNT is the use of transition metal oxide nanoparticles as catalytic growth sites for the CNT, which results in metallic residues within the final product as contaminants. Recently, it has been reported that CNT can be

grown from silica nanoparticles in lieu of metal oxide particles, which promises to yield CNT completely free of metallic particulate contaminants.^[7,8] An alternative synthetic approach is the development of wet-chemical synthetic routes to these materials, potentially mirroring the widespread success of such techniques in the petrochemical and pharmaceutical industries. Although bench-top, open-vessel synthetic chemistry has yet to produce nanostructures such as CNT or fullerenes, there are several reports of solvothermal^[9] and hydrothermal^[10] syntheses of various carbon nanostructures and even graphene.^[11] For example, Hu et al.^[12] produced multiwalled CNT (MWCNT) in a solvent-based reaction in the presence of a NiO catalyst and variations of this basic approach have also been reported.^[9,13,14] Advances in the chemical synthesis of nanomaterials are primarily aimed at lowering the reaction temperature and the elimination of the need for catalysts, with the aim of making the bulk synthesis of such materials more economically viable and facilitating the incorporation of the materials into commercial applications. A further advantage of metal-catalyst-free synthetic routes is the absence of metallic or metal oxide particulate impurities in the final carbon materials, which are otherwise very difficult to remove without otherwise affecting the properties. Further to this, we have developed reaction pathways to MWCNT and carbon nanospheres at unprecedentedly low temperatures, in the complete absence of transition metal catalysts. The MWCNT were produced in solvothermal reactions at 190°C, whereas the nanospheres resulted from reactions

occurring at atmospheric pressure and 100°C. These new reactions represent a significant advance in the scope to incorporate such materials into composites and for applications that require high-surface-area substrates such as catalytic supports or purification technologies.

Experimental

Materials

All reagents used in the synthesis were of reagent grade and were used without further purification. X-ray photoelectron spectroscopy (XPS) was performed on an Escalab 220i XL instrument using a monochromated Al K_{α} X-ray source ($h\nu = 1486.6$ eV) operated at 10 kV and 12 mA. The pressure in the measurement chamber was typically $\sim 1 \times 10^{-9}$ Torr and samples were mechanically secured into aluminium holders for measurement. A region of ~ 4 mm² was examined during each measurement and several regions on each sample were investigated to ensure sample uniformity. The step size in experiments was either 1 eV (wide scans) or 0.1 eV (high-resolution region scans) and Varian *Eclipse V.2* software was used for data processing. Scanning electron microscopy (SEM) was conducted on a Hitachi S900 field-effect scanning electron microscope (4 kV). Transmission electron microscopy (TEM) was conducted on a Phillips CM200 (200 kV) and a JEOL1400 (100 kV). Nitrogen adsorption isotherms were measured at 77 K on a Micromeritics ASAP 3020 over the range pressure range $2 \times 10^{-5} < P/P_0 < 0.98$, where P_0 is the atmospheric pressure and P is the applied pressure. Samples were degassed at 150°C and 5×10^{-5} Torr for 24 h before adsorption analysis.

Solvothermal Synthesis

Hexachlorobenzene (HCB) (1.050 g, 3.69 mmol) and metallic sodium (0.959 g, 41.71 mmol) were placed in a Teflon-lined Parr reactor vessel (23 mL internal volume, model no. 4749) with cyclohexane (12 mL) as a solvent. The autoclave was sealed and placed in a furnace (220°C) for 18 h, after which the reaction vessel was removed and allowed to cool to room temperature. In the event of there being residual HCB present (easily identified as white needle-like crystallites), the bulk, mostly black product, was broken up with a spatula, resealed, and heated once more for another 12 h; this process was repeated until such time as no further HCB was observed. On cooling, excess ethanol was added to the mixture, which was then left to stand for 4 h in order to consume any remaining sodium metal. The sample was then filtered by vacuum filtration and washed

with a sequence of ethanol, hot ethanol, hot ethanol/water, hot water, hot ethanol, hot cyclohexane, ethanol, water, and finally with hot ethanol. The washed sample was dried in a vacuum for 2 h at 150°C, yielding the final product (0.273 g), representing 84.3 % yield based on a final sample composition of 88.2 atom-% carbon, as observed in the XPS data.

Production of Highly Porous Carbon Spheres

A reaction mixture of HCB (7.356 g, 25.83 mmol), metallic sodium (3.787 g, 164.7 mmol), and toluene (50 mL) was stirred with a magnetic stirrer under an inert nitrogen atmosphere under reflux ($\sim 110^\circ\text{C}$) for ~ 45 min. Ethanol was added in order to consume any remaining sodium before washing the product with toluene, ethanol, an ethanol/water (1 : 1) mix, water, and finally ethanol. The washed sample was dried in a vacuum at 120°C for 3 h, yielding the final product (1.286 g), representing 57.2 % yield based on a final sample composition of 88.1 atom-% carbon, as observed in the XPS data.

Results and Discussion

The solvothermal reaction produced largely CNT bundles, characterised using SEM, XPS, and TEM. TEM images of the CNT bundles show that the bulk of the tubes were aligned in parallel and have a distinct face (Fig. 1). Sonication of the samples in ethanol for 5 min before imaging with TEM was found to partially disperse the bundles into individual tubes; prolonged sonication resulted in almost complete disintegration of the bundles into individual CNT. This relatively mild treatment indicates that the CNT produced are strongly bonded along the tube, but relatively weakly held by dispersive forces into bundles. By imaging many samples, the maximum bundle lengths were observed to be ~ 80 μm , ($\alpha \approx 10^4$ for individual CNTs). However, the diameters of the tubes in any given sample were found to not be uniform, with tubes of the smallest diameter of 5 nm and the largest observed diameter of 100 nm.

SEM images highlight the high yield of CNT; on the basis of these SEM observations, the CNT represent $\sim 80\%$ of the carbon in the sample, with the remainder of the sample containing other forms of graphitic or disordered, amorphous carbon (80 % is an estimation based on the carbon structures observed in the SEM images). The accepted growth mechanism of CNT is via either tip or base growth from catalytic nanoparticles, usually transition metal oxides.^[15] In this case, there was no addition of any transition metals; however, the sodium was

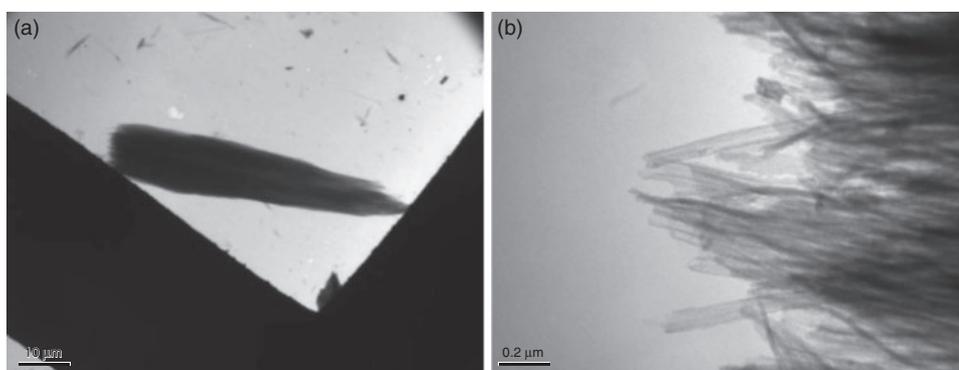


Fig. 1. Agglomerated carbon nanotubes: (a) under low magnification (2500 \times), a single large piece >50 μm is observed; (b) under higher magnification (10⁵ \times), the left-hand edge of the same sample region shows that it consists of individual carbon nanotubes. The black regions in (a) are due to the Cu grid used as a sample substrate.

allowed to partially oxidise in air or under a volatile solvent such as cyclohexane. When the experiment was repeated in the complete exclusion of oxygen, we observed longer reaction times and lower CNT yields. It is therefore natural to postulate that the CNT grow off the surface of the sodium, using the oxide layer, or even sodium chloride particles, as nucleation sites or growth catalysts rather than transition metal oxide particles. This is supported by the SEM observation of flat surfaces on some of the bundles (Fig. 2); however, it must be noted that no residual sodium was observed in the final product owing to the post-synthetic washing, which removes sodium and its salts. Other researchers have recently noted the growth of CNT off nanoparticles other than transition metal oxides, such as on appropriately sized SiO_2 , providing additional support for this more general CNT growth model.^[7,8]

The reaction was repeated in a 125-mL titanium Parr reactor (model no. 4750), resulting in the same products, and thus demonstrating a scalability factor of 5. The effects of reaction temperature were also investigated; reactions performed below 190°C failed to yield any CNT, whereas the CNT obtained at 190°C were less well defined than those obtained at 220°C. An upper reaction temperature limit of 220°C was used in order to obtain reasonable quality CNTs, but also as a safety measure given that the autoclaves were limited to $T < 250^\circ\text{C}$ and that the localised heating within the reaction mixture could not be determined directly. XPS of the typical CNT samples indicated that the solid is predominantly carbon; normalised peak areas related to the elemental composition (in atomic-%) were determined to be: Na 0.305, O 8.61, C 88.71, and Cl 2.37 %.

In addition to the MWCNT, a highly porous carbon consisting of spheres, or bubbles, was produced from the refluxed reaction of HCB and sodium in toluene ($\sim 110^\circ\text{C}$). The resultant dried bulk powder is a very fine, low-density solid that is almost liquid-like in flow. The TEM images indicate that the sample consists of bubbles, fused together to form a foam-like material. It was also noted that individual bubbles could be separated from the bulk under sonication (Fig. 3), resulting in discrete bubbles as small as 50 nm. In addition, the TEM studies also provide some insight to the permeability of the carbon nanobubbles; as the spheres form in solution, each bubble or sphere may reasonably be expected to contain encapsulated solvent. However,

given that the bubbles remained intact after drying under a vacuum at 120°C, it appears that the surface of the bubble is permeable to the solvent, in this case toluene, preventing rupture of the walls and thus maintaining the integrity of the spheres. However, it must be noted that one or two of the bubbles were observed to rupture under the focussed electron beam of the TEM, assumed to be owing to the rapid heating of encapsulated solvent remaining after drying; this behaviour was exceptional, however, with most bubbles remaining intact even under the focussed 200-kV electron beam.

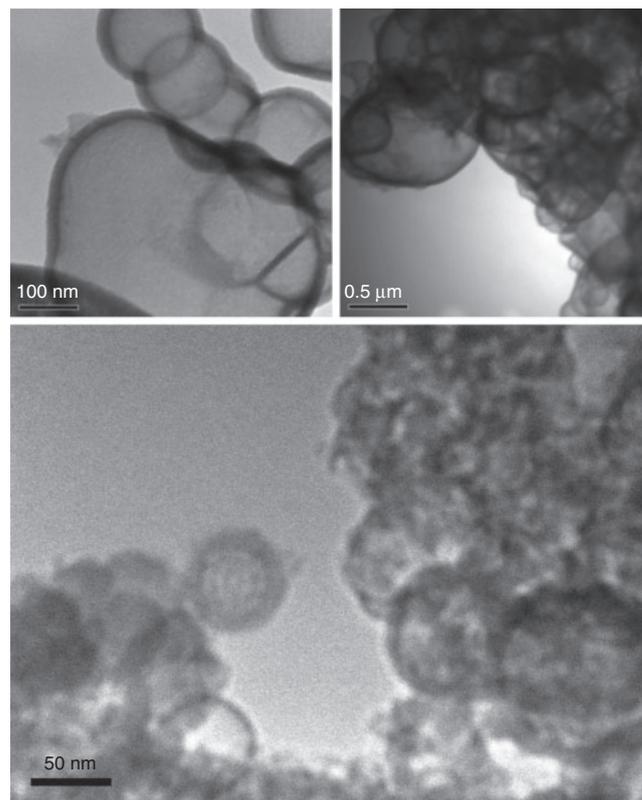


Fig. 3. Transmission electron micrographs of the carbon nanobubbles.

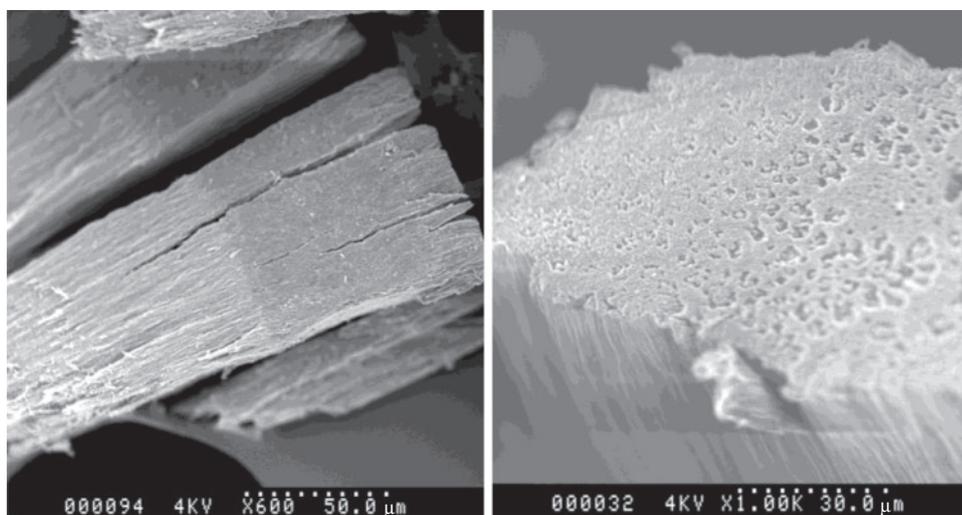


Fig. 2. Two scanning electron microscopy images of bundles of carbon nanotubes that are truncated at planes, alluding to the growth of the bundles being via a surface.

The XPS analysis of the bubbles confirms the complete absence of any transition metal or solvent residues, with the typical composition being (atomic-%): Na 0.543, O 10.11, C 88.09, and Cl 1.256 %.

The Brunauer-Emmet-Teller (BET) specific surface areas (Table 1) for the synthesised MWCNTs ($987 \text{ m}^2 \text{ g}^{-1}$) are higher than for reported MWCNT ($307.7 \text{ m}^2 \text{ g}^{-1}$)^[16] and even above reported single-walled carbon nanotubes (SWCNT) ($854 \text{ m}^2 \text{ g}^{-1}$)^[17] and have a comparably high hydrogen adsorption for such low pressures for MWCNT (0.71 wt-%)^[16] but not SWCNT (<2.5 wt-%)^[17]. Meanwhile, the nanobubbles exhibited a lower BET surface area, but a significantly increased micropore contribution; however, compared with other activated or porous carbons, they do not perform well for surface area or hydrogen adsorption.^[16,17] The H_2 enthalpy of adsorption is within the expected range for a carbon material; notable, however, is the sustained adsorption enthalpy with increasing H_2 coverage for the nanobubbles. This finding is commensurate with the substantial microporosity recorded in this material (Table 1), which provides enhanced overlap of surface potential energy wells within the narrow pores, and hence enhanced physisorption. Confirmation of this structure was found from micropore size analysis (Dubinin–Astakhov, Fig. 4 inset), which revealed a distribution centred at 16.5 \AA . It has been noted that the treatment of MWCNT in alkaline conditions, such

as those encountered in the purification steps of the present synthesis, may result in higher degrees of hydrogen adsorption,^[16] which may also be a factor in the greater H_2 loading of the MWCNT over the nanobubbles.

We have demonstrated that CNT growth does not require transition metal catalysts in a solvothermal reaction of metallic sodium with HCB. However, as higher CNT yields were achieved in the presence of mildly oxidised sodium surfaces, the role of an oxide layer in the formation of CNT appears to be significant, presumably assisting in the carbon dispersion into a eutectic before phase separation on growth. The synthesis of MWCNT on potentially large scales with relatively simple apparatus provides a viable treatment method for HCB, a persistent halogenated waste, highly toxic to human and marine life^[18] and controlled under the Stockholm Convention.^[19] The relatively low cost of sodium and short processing time, coupled with the commercial value of CNT, makes this method of HCB remediation preferable to high-temperature incineration, particularly in countries in which no commercial high temperature incineration facility exists and for which transfer of the material may contravene international conventions. With the only by-product being NaCl and significantly reduced direct carbon emissions – the incineration of HCB results in the emission of a mass of CO_2 approximately equal to that of the initial HCB waste – this chemical approach is a viable commercial alternative to incineration techniques currently required in the destruction of such pollutants.

Table 1. Structural characteristics resulting from gas adsorption measurements

	$\text{SA}_{\text{BET}}^{\text{A}}$ [$\text{m}^2 \text{ g}^{-1}$]	Total pore volume ^B [$\text{cm}^3 \text{ g}^{-1}$]	Micro- pore area ^C [$\text{m}^2 \text{ g}^{-1}$]	H_2 uptake [wt-%] ^D	ΔH_{ads} [H_2 , kJ mol^{-1}] ^E
Nanobubbles	685	0.49	226	0.87	8.53–5.44
Nanotubes	987	1.36	44	0.99	8.69–4.71

^ACalculated from application of the BET equation over the range $0.05 < P/P_o < 0.35$.

^BMeasured at $P/P_o = 0.98$.

^CObtained from t -plot analysis.

^DMeasured at 118.55 kPa and 77 K.

^EMeasured from Van't Hoff plots applied to isotherms measured at 77 and 87 K.

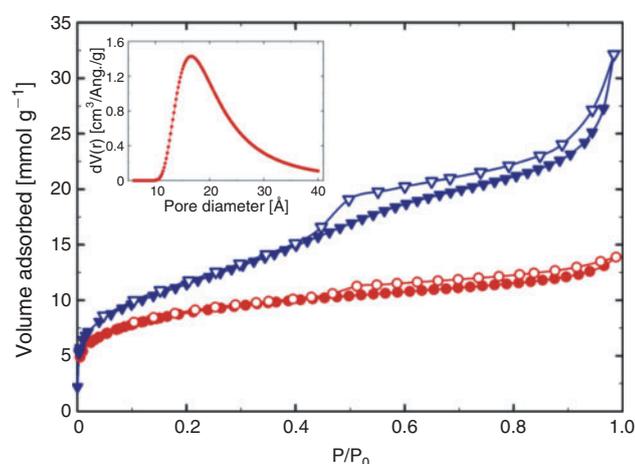


Fig. 4. Nitrogen isotherm at 77 K of nanobubbles (circles) and nanotubes (triangles). Adsorption: solid symbols; desorption: open symbols. Inset: Dubinin–Astakhov micropore distribution for nanobubbles.

Conclusion

The production of CNT at low temperatures in a simple wet-chemical reaction without the need for transition metal catalysts has been demonstrated. The large bundles of tubes show huge potential for scalable mass-production of CNT, potentially a cheap, high-purity (with respect to the absence of transition metal particles), and high-aspect-ratio raw material for carbon yarn drawing,^[20] where both the length and purity are critical considerations in obtaining high-quality yarns. In addition, we also produced carbon nanobubbles in similar reactions under atmospheric pressure; although these materials may not immediately hold as much interest as the MWCNT, the relative ease and lower cost of treatment may render this a more favourable remediation technology than the solvothermal reaction. Given the practical realities of the environmental clean-up of polychlorinated aromatics such as HCB – cost, public opinion, availability of processing options, transportation, and international law – this innocuous approach provides a workable alternative that is able to bypass each of these practical challenges.

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References

- [1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, 318, 162. doi:10.1038/318162A0
- [2] V. Shanov, A. Gorton, Y. Yun, M. Schulz, *US patent US2008/0095695 A1* **2007**.
- [3] S. Iijima, *Nature* **1991**, 354, 56. doi:10.1038/354056A0

- [4] C. Journet, W. Maser, P. Bernier, A. Loiseau, M. L. de la Chapelle, S. Lefrant, P. Deniard, R. Lee, J. E. Fischer, *Nature* **1997**, *388*, 756. doi:10.1038/41972
- [5] M. Yudasaka, T. Komatsu, T. Ichihashi, S. Iijima, *Chem. Phys. Lett.* **1997**, *278*, 102. doi:10.1016/S0009-2614(97)00952-4
- [6] M. José-Yacamán, M. Miki-Yoshida, L. Rendon, J.G. Santiesteban, *Appl. Phys. Lett.* **1993**, *62*, 202. doi:10.1063/1.109315
- [7] S. Huang, Q. Cai, J. Chen, Y. Qian, L. Zhang, *J. Am. Chem. Soc.* **2009**, *131*, 2094. doi:10.1021/JA809635S
- [8] B. Liu, W. Ren, L. Gao, S. Li, S. Pei, C. Liu, C. Jiang, H.-M. Cheng, *J. Am. Chem. Soc.* **2009**, *131*, 2082. doi:10.1021/JA8093907
- [9] Y. Jiang, Y. Wu, S. Zhang, C. Xu, W. Yu, Y. Xie, Y. Qian, *J. Am. Chem. Soc.* **2000**, *122*, 12383. doi:10.1021/JA002387B
- [10] Y. Gogotsi, J. Libera, M. Yoshimura, *J. Mater. Res.* **2000**, *15*, 2591. doi:10.1557/JMR.2000.0370
- [11] M. Choucair, P. Thordarson, J. A. Stride, *Nat. Nanotechnol.* **2009**, *4*, 30. doi:10.1038/NNANO.2008.365
- [12] G. Hu, M. Cheng, D. Ma, X. Ba, *Chem. Mater.* **2003**, *15*, 1470. doi:10.1021/CM0209362
- [13] T. Luo, L. Chen, K. Bao, W. Yu, Y. Qian, *Carbon* **2006**, *44*, 2844. doi:10.1016/J.CARBON.2006.03.020
- [14] Y. Yan, H. Yang, F. Zhang, B. Tu, D. Zhao, *Carbon* **2007**, *45*, 2209. doi:10.1016/J.CARBON.2007.06.049
- [15] Y. Li, W. Kim, Y. Zhang, M. Rolandi, D. Wang, H. Dai, *J. Phys. Chem. B* **2001**, *105*, 11424. doi:10.1021/JP012085B
- [16] C.-H. Chen, C.-C. Huang, *Int. J. Hyd. Energy* **2007**, *32*, 237. doi:10.1016/J.IJHYDENE.2006.03.010
- [17] B. Panella, M. Hirscher, S. Roth, *Carbon* **2005**, *43*, 2209. doi:10.1016/J.CARBON.2005.03.037
- [18] M. Eggesbø, H. Stigum, M. P. Longnecker, A. Polder, M. Aldrin, O. Basso, C. Thomsen, J. U. Skaare, G. Becher, P. Magnus, *Environ. Res.* **2009**, *109*, 559. doi:10.1016/J.ENVRES.2009.04.001
- [19] *Stockholm Convention on Persistent Organic Pollutants*. **2009** (Secretariat of the Stockholm Convention). Available from: <http://chm.pops.int/Convention/ConventionText/tabid/2232/Default.aspx> (accessed August 2013).
- [20] N. Behabtu, C. C. Young, D. E. Tsentelovich, O. Kleinerman, X. Wang, A. W. K. Ma, E. A. Bengio, R. F. ter Waarbeek, J. J. de Jong, R. E. Hoogerwerf, S. B. Fairchild, J. B. Ferguson, B. Maruyama, J. Kono, Y. Talmon, Y. Cohen, M. J. Otto, M. Pasquali, *Science* **2013**, *339*, 182. doi:10.1126/SCIENCE.1228061