Nanotechnology for military applications

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This paper examines some of the ways in which nanotechnology could be applied to enhance military ordnance, especially explosive devices propelled through the air, which makes any substitution that reduces weight of especial interest. Specific topics covered include propellants and explosives, optical materials, and materials for energy storage, heat management etc. The paper also discusses some of the practicabilities of procuring technology from the civilian market, and provides a useful update of the scheme of technology readiness levels used to classify new and emerging technologies, proposing *nanotechnology availability levels* for use specifically with nanotechnology.

1. Scope

Military history is peppered with examples of lightly armed armies besting heavily armed opponents, by virtue of the superior mobility and speed of response conferred by the light weaponing. Every English schoolboy knows that the battle of Agincourt in 1415 was won by the English because of the decisive superiority of their light longbows, an innovative, superior technology in comparison with the powerful but heavy crossbow favoured by the French. Even the much earlier (*ca* 1000 B.C.) story of the lightly armed, hence agile, David beating the lumbering Goliath illustrates this general principle at the level of the individual warrior; the innovation of the battlecruiser, championed by Admiral Fisher at the beginning of the 20th century, versus the heavier, slower battleship may be considered as yet another example. Seen in this light, nanotechnology is simply the latest means whereby military ordnance can be reduced in size and weight while keeping the same performance or even enhancing it. The potential military applications of nanotechnology cover almost every aspect, ranging from essentially civilian applications such as ultralight clothing and footwear for an individual warrior to the sophisticated information-processing electronics that are embedded in almost everything (and which, nowadays, are mostly sourced from the civilian market). This review concentrates mainly on flying weapons—missiles—for it is here that the benefits of size and weight reduction are especially advantageous.

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Nanotechnology is succinctly defined as "engineering at the nanoscale" (a more complete definition is given in Section 3). For hundreds of years mechanical and, later, electrical engineering have been concerned with miniaturization; part of nanotechnology is simply a continuation of this miniaturization from the now well-established microsystems technology (MST), which encompasses materials and devices with feature sizes of 1–10 μm, down to the nanoscale (less than 100 nm). As well as this incremental or "soft" aspect there is also a revolutionary or "hard" one involving completely new materials with no larger counterpart, such as the recently discovered "nano" forms of carbon, namely fullerenes, nanotubes and graphene.

The emphasis in this paper will be on the "soft" (near- and medium-term) technology, which already exists in concrete form, at least in a research laboratory and perhaps as a commercial product in a non-military domain. "Hard" assembler-based nanofacture and productive nanosystems based on assemblers, which must be considered a long-term development, are excluded.

Generic aspects of nanotechnology, in particular nanometrology and the modelling of nanomaterials and nanodevices, are excluded. The main tools for structural characterization (including electron ultramicroscopy in its various forms and scanning probe ultramicroscopies) are well developed with many decades of research behind them, and will continue to play a supporting role, as will atomic-scale modelling—heavily reliant on powerful digital computers, whose processor chips are themselves already nano-enabled nowadays.

Some parts of what are nowadays sometimes considered to be nanotechnology (e.g., the fabrication of ultrafine particles) have a history going back centuries, if not millennia. In these cases we have merely had a relabelling. "Top-down" fabrication has a history of steady miniaturization, starting two or three centuries ago. Such fabrication constitutes the main parts of nanotechnology currently within industrial practice (including composites). It is typical of the intermediate situation in which we currently find ourselves that nanotechnology can sometimes be used to enhance "subnano" technologies (i.e., finished with a precision lower than that of nanotechnology), the need for which will ultimately disappear. Here is a tribology example. If machining can routinely achieve a surface roughness of 1 nm combined with ultrahardness, lubricants may not be necessary, but as long as surfaces are still rougher or softer, nano-engineered lubricants (e.g., the Au/MoS_2 solid lubricant films developed by the Aerospace Corporation in California [30]) offer better performance than conventional lubricants. Other examples of such intermediate or bridging technologies are to be found in the field of thermal management.

This review is divided into four parts. Sections 1 and 2 contain introductory material; Section 3 deals with readiness and availability, Section 4 with timescales, Sections 5 and 6 with, respectively, where research and supply partners may be found, Section 7 with propellants and explosives, Sections 8 and 9 with, respectively, electrical and optical applications, Section 10 with other materials and the final Section 11 carries the conclusions.

2. Definition of nanotechnology

Nanotechnology is defined as "the deliberate and controlled manipulation, precision placement, measurement, modelling and production of matter in the nanoscale in order to create materials, devices, and systems with fundamentally new properties and functions" [2]. "Create" is usually interpreted as encompassing design and fabrication. It follows that it has three aspects:

1. A universal fabrication procedure;
2. A particular way of conceiving, designing and modelling materials, devices and systems, including their fabrication (which bears the same relation to classical engineering as "pointillisme" does to classical painting);
3. The creation of novelty.

The fabrication aspect (1) has three subaspects:

1. "Top-down" (exemplified by ultraprecision machining and semiconductor processing);
2. "Bottom-to-bottom" (assemblers);
3. "Self-assembly" ("bottom–up", much of which is bio-inspired).

The concrete (fabrication and design) aspects of the entire field of nanotechnology are captured by Scheme 1. As for the novelty (aspect 3), this is exemplified by:

1. Objects with no bulk counterpart (e.g., carbon nanotubes);
2. Objects acquiring new functionality because of their nano-enabled ultrasmall size or cost (implying the possibility of vast numbers);
3. Enhanced performance, including the achievement of novel combinations of properties by bringing nanoscale components together in intimate juxtaposition.
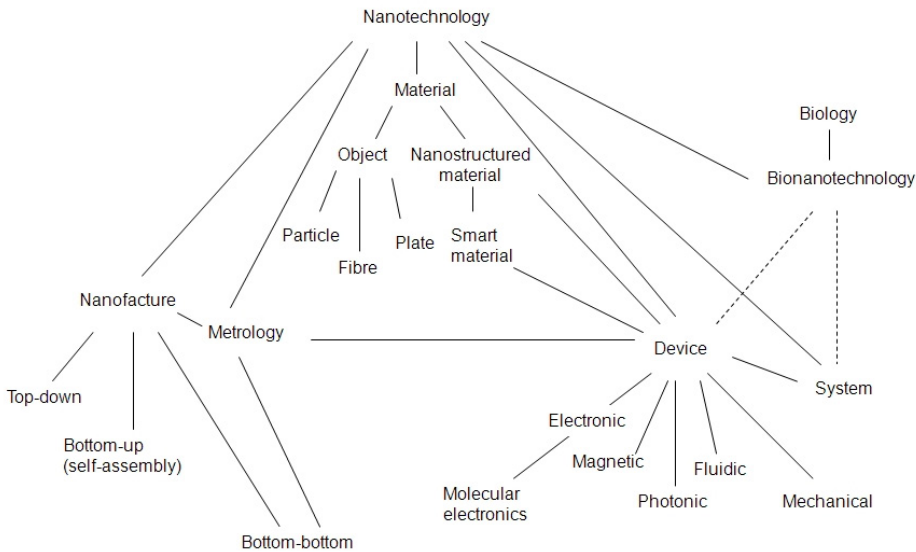
Scheme 1. Outline of a concept system (ontology) for nanotechnology. Most of the terms would normally be prefixed by "nano" (e.g., nanometrology, nanodevice). A dashed line merely signifies that if the superordinate concept contributes, then the prefix should be further modified accordingly (e.g., bionanodevice, bionanosystem). Biology may also have some input to nanomanufacture (nanofacture), inspiring, especially, self-assembly processes. Reproduced with permission from [45].

Note that the definition at the beginning of this section refers to the nanoscale, which, therefore, also needs definition. Because nanotechnology covers so many different aspects, for each of which a particular nanoscale could be defined [47], a consensus has been reached by the International Standards Organization (ISO), according to which the range 1–100 nanometres is fixed as constituting the nanoscale.

Nanoscience, by the way, is defined as the science necessary for achieving nanotechnology, which has itself a purely practical aim.

3. Technical and commercial readiness (availability) levels

The notion of technology readiness level (TRL) originated in the NASA Advanced Concepts Office [35]; it was specifically designed to characterize the progress of technologies used in space missions. Despite this association with a very closed and controlled uncommercial environment, it has since then been widely adopted to characterize general industrial technologies, for which it is not wholly appropriate. Hodgkinson et al. proposed modifications to render it more suitable for general use (Table 1) [23]; we might name the modified scheme "commercial readiness levels" (CRL). The third column in Table 1 has been added to characterize the nature of the activity culminating in the achievement of each level. "Science" means here "research"; that is, the application of the scientific method to make discoveries and create new knowledge; and "engineering" means "development"; that is, the application of existing knowledge to perfect something in order to enable it to deliver practical, useful results [46]. Of course, many new things are also discovered during development but the work is directed towards a specific goal, whereas science is open-ended. Science can be considered to have become technology by TRL 4 or 5.

Table 1. Technology or commercial readiness levels (after Mankins [35] and Hodgkinson et al. [23]). The third column identifies the nature of the work involved in arriving at that level.

T(C)RL	Description	Nature[a]
1	Basic principles observed	S
2	Proof of concept	S
3	Technology application formulated	S/E
4	Component validation in the laboratory environment	S/E
5	Component validation in the real environment	E
6	Prototype system demonstration in the real environment	E
7	Commercial introduction	E
8	Commercial success	E

[a] Science (S) or engineering (E).

Even the modified scheme of CRL is, however, inadequate to represent the progression of nanotechnology, because of some unique features, especially its extremely rapid progression and the intermingling of academic and industrial research. Hence, a scheme of *nanotechnology availability levels* (NAL) is proposed here to more accurately describe the state of a given part of nanotechnology with respect to the desired application (Table 2).

Note that in any technical development project the levels may not be ordered in a strict sequential hierarchy: NAL 4 may well accompany NAL 3; availability at NAL 5 may only be of research grade material. Levels 0 to 6a would typically be reached in the research environment; levels 0–3 might well be carried out in an academic environment; while institutes of technology might continue work through levels 4 and 5, possibly then transferring operations to a spin-off company in order to progress the technology further. NAL 6a corresponds to the interest of the supplier and ultimate manufacturer; NAL 6b and 7b are in the interest of the ultimate end-user,

Table 2. Nanotechnology availability levels (NAL), giving next
step requirements (NSR).

NAL	Description	NSR[a]
0	Idea	Rl
1	Basic principles observed	R1,V
2	Proof of concept	I
3	Technology application(s) formulated	IP, R2
4	Demonstration for some specific application	P
5	Available in some form	St
6a	COTS availability	R3,SC
6b	Validated for a desired application	SC
7a	Complete supply chain established	R4
7b	Incorporated into the product	U,R4
8	History of success	R4

[a] Key to next step requirements (NSR):

R1 Exploratory laboratory work
V   Verification
I   Inspirational thinking
IP Patent application
P   Development of a feasible production route
R2 Research to establish whether the technology can be used for the desired
     application and whether it is superior to existing technology
St Standardization
R3 Testing in the desired application
U   Use
SC Establishing the supply chain
R4 Optimization

which is likely to have to shoulder the burden of the research work labelled R3. 6a and 6b are likely to take place in parallel; likewise for 7a and 7b. Ongoing R4 is generally required for sustainable deployment. Nowadays it is common for academic laboratories to seek to patent new technologies, which introduces some friction into the reporting—a published account of the principles (NAL 1) may only appear after levels 4 and 5 have been reached.

Level 7a can be further divided into the following *maturity levels* (taken from the International Technology Roadmap for Semiconductors, ITRS):

7a.1. Manufacturable solutions are not known
7a.2. Interim solutions are known
7a.3. Manufacturable solutions are known
7a.4. Manufacturable solutions exist and are being optimized.

Level 7b could already begin to be accessed once Level 7a.2 or 7a.3 is reached.

Nanotechnologies that can meet short-term needs in a particular area have typically already been developed for some other application (i.e., NAL 3 or 4). Given that the material is available in some form, it is essentially a matter of straightforward engineering development to adapt it for the new requirement, without excluding the possibility that unexpected problems arise needing more fundamental investigation of, probably, a very specific aspect. Short-term technologies already have some commercial activity, which may not be in the same area of application as the one of interest. Medium-term technologies are being actively pursued in university and other academic laboratories as well as in the research laboratories of leading high technology

industries (although activity in the latter is usually only revealed when a patent application is filed). Long-term technologies are currently less actively pursued in academic laboratories than might be imagined (because they are increasingly forced to rely upon short-term research contracts with government funding agencies that require detailed, prespecified outputs unsuited to the pursuit of "blue skies" research); the main thrust is currently from privately funded nonprofit institutions and theoretical work by academics not forced to rely on external funding.

Note the deliberate alignment of the TRL, CRL and NAL. Therefore, in every case the actual numbers should convey roughly the same meaning.

Manufacturability. It should be borne in mind that the ultimate goal of most nanotechnology research is high-volume, low-cost manufacture of a material or device. It seems that none, or hardly any, of the great number of research papers published each year address this issue. Single electron devices and the like tend to be a *tour de force* of individual skill and ingenuity, but there is no clear route thence to the higher availability levels. Unfortunately, even the more detailed and better adapted (compared to TRL or CRL) NAL do not capture the possibility of an intrinsic limitation to the new technology that will prevent it ever getting beyond level 3. Manufacturability, therefore, needs careful attention that will probably require customized analysis, especially since it is not usually addressed in the literature (ref. [26] is a notable exception).

4. Predicting development timescales

Such prediction is difficult for new technologies because they progress exponentially; the best known example of such progression is probably Moore's law, which states that the number of components on a VLSI chip doubles every 18 months. Hence, if we now have 10^9 components on a chip, we can expect there to be $2^6 \times 10^9$, or almost 10^{11}, components after nine years (this does not necessarily imply that performance is 100 times better, because programming abilities to exploit the increased number of components typically lag behind). This kind of prediction of exponential development can only be made with some hope of reliability when an entire industry is taken into consideration. The rate of development in a narrow field is much harder to predict. It usually depends strongly on the volume of available resources, especially manpower. Furthermore, discoveries in other, seemingly unrelated, fields may solve bottlenecks and have other dramatic, unpredicted effects; in industries such as pharmaceuticals with strong regulatory controls, the need to fulfil extensive and exhausting tests before commercialization means that any innovation, whether involving nanotechnology or not, may take as long as 15 years to reach the market.

Short-term (< 5 years) needs are typically met by substitution of a traditional material or extant device (which might already be micro) by nanotechnology. In simple cases, there is a clearly predictable benefit (e.g., less cost for the same performance, or more performance for the same cost). In more complex cases, there is a trade-off; if benefits and disbenefits are size-dependent but the dependences are of opposite sign, there will be a definite characteristic size (crossover point) below which there is no advantage to be gained. This applies, for example, to microelectromechanical systems (MEMS) used, e.g., as inertial sensors such as accelerometers; performance is degraded upon miniaturization down to the nanoscale.

Short-term applications need essentially development, including optimization, of existing technologies. The technologies may have been developed with other purposes in mind, in which case adaptation to the specific need is required. Computer modelling may be brought to bear if

experiments are difficult, in order to narrow the scope and reduce the required number of experiments. In all these applications, the first step must be to draw up detailed specifications of what is required. Available knowledge can then be used to select candidate solutions, and the final choice must depend on comparative experiments.

Although at first sight there seems to be a plethora of nanomaterials ripe for short term applications (beyond niches such as tennis balls and racquets and stain-proof cravats), the lack of standardization of raw materials is a definite handicap. Research work, therefore, has to rely on the material produced by a particular supplier, with no guarantee that the results can be used with materials from other suppliers (even if the material is nominally the same). If the research is successful and the material is shown to be fit for purpose, a similar difficulty arises at the next level because of the fragility of any supply chain depending on a single manufacturer. That is why the introduction of exchange-based trading of commoditized nanomaterials is a prerequisite for sustaining short-term development into the medium and longer terms (cf. Section 6).

Medium-term (5–15 years) applications require research (of type R2 according to Table 2)—comprising both experimental and more or less profound theoretical analysis—in order to be able to appraise the practicability of selecting the technology for development.

The long-term (> 15 years) applications of nanotechnology, apart from those listed in the previous section that belong to the far end of the medium term, are essentially associated with the development of nanoscale assemblers (also known as bottom-to-bottom "fabbers", mechanosynthesizers, etc.) as universal fabrication tools, as was suggested by R.P. Feynman in a lecture given in 1959 at Caltech and later developed in much more detail by K.E. Drexler, R.A. Freitas Jr, R.C. Merkle and others. Although assemblers would therefore appear to constitute the very centre of the mainstream of nanotechnology, and although the US National Nanotechnology Initiative (NNI) launched in 2001 makes strong reference to Feynman, that initiative has ended up giving very little support to the development of bottom-to-bottom fabrication, which is, therefore, nowadays carried out in small number of university or private institutions such as the nonprofit Institute for Molecular Manufacturing in Palo Alto. A similar situation prevails in Europe: in the UK, for example, only one research group (that of Philip Moriarty at the University of Nottingham) is apparently giving serious attention to the problem, which is not a favoured topic for the Engineering and Physical Sciences Research Council (EPSRC), despite nanotechnology being one of its priority areas. The situation in China is not reliably known. Given this starvation level of support, it is not surprising that progress is rather slow, especially on the experimental front. Note, however, that once a working assembler is built, given its capability of building other assemblers, the technology will then spread exponentially.

5. Locating research partners

The premiss here is that it may be cost-effective to outsource research but development will be done in-house. It is often sufficient to confine one's attention to the USA, Japan and technologically leading European countries (France, Germany, Switzerland, the UK).[1] Typical government policy regarding nanotechnology is to enable worthy but laggard institutions to

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[1] Other countries are also making significant contributions, especially the Netherlands and Belgium, Denmark, Sweden and Finland, and Hungary.

catch up with their peers—this is an especially strong feature of the US National Nanotechnology Initiative. It is not, therefore, the case that a handful of institutions are producing the overwhelming bulk of the exploratory research; important innovations are widespread. Sheer size plays a role; a small university may achieve international prominence in only one small niche area. Where spin-out activity is strong, as in Switzerland, the technology may already be in the commercial realm by the time it gets reported and an end-user may find it more expedient to collaborate with the spin-out company rather than the university research group in which the technology initially originated. Many microcompanies have a single highly innovative product protected by a key patent.

The general level of technological infrastructure plays a vital role beyond the lowest levels of technological achievement. For this reason, Russia is not a prominent player because, although new ideas might still be originating there, it is not possible to take them very far without overseas collaborations, thanks to the effective dismantling of the science base following the demise of the Soviet Union. The biggest unknown quantity is China (that is, wholly Chinese enterprises rather than joint ventures or subsidiaries of foreign companies). The scientific literature reveals a tremendous volume of nanotechnology work going on there at both research and development levels [28], albeit of widely varying quality, but it is less certain whether reliable supply partners can be found.

The most prolific institutions in the world are umbrella organizations comprising many individual institutes: the Chinese Academy of Sciences, the Russian Academy of Sciences, the Centre National pour la Recherche Scientifique in France, in places 1, 2 and 3 respectively for producing the most nanotechnology papers in 2005 [28]. France is relatively outstanding: the comparable Consiglio Nazionale per la Ricerca in Italy only produces about two thirds of the output (and appears in rank 13). Position 4 is occupied by Tsing Hua University in China, and the next three positions by Japanese universities (Tohoku, Tokyo and Osaka). The list is indeed dominated by the Far East. The most prolific institution in the USA is the University of Illinois (rank 17); there are only two other US universities (Berkeley and Texas) in the first 30. The only European university is Cambridge (rank 24); the Indian Institutes of Technology (another umbrella organization) only appear at rank 28. Recently the Rensselaer Polytechnic Institute (NY) has reported several significant discoveries in areas likely to be of interest to readers of this review. Other key nanotechnology centres in Japan are the Tokyo Institute of Technology, Kyoto University, Ritsumeikan University, the National Institute for Materials Sciences (NIMS), RIKEN and AIST.

Nowadays, with an unprecedented level of global networking and the highly efficient dissemination of knowledge (thanks to excellent communications) , it is not a difficult problem to find a laboratory capable of carrying out almost any kind of nanotechnology research. Many, many universities and similar academic institutions are carrying out some work on nanotechnology. Facilities might be a limiting factor—even today, no single institution appears to have all that is required to undertake *any* kind of nanotechnology work, but if money is no obstacle equipment can be acquired, and specialized technical expertise is mobile.[2]

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[2] As an extreme example, in 2009 an entire research-intensive university was created *ex nihilo* on a desert shore where only a few fishing villages existed beforehand (the King Abdullah University of Science and Technology, KAUST). It is, however, too early to assess the success of this venture. Note that nanotechnology is one of its six priority areas.

Within the UK, the obvious centres of excellence for nanotechnology include the BAE Systems Advanced Technology Centre (ATC) at Filton and Qinetiq Advanced Microsystems Engineering at Malvern. Many universities are conducting some kind of nanotechnology research; the top four universities with respect to patenting activity are Cambridge, Oxford, Glasgow and Imperial College (London).

Globally, leading nanotechnology companies (i.e., large companies that have made a serious commitment to nanotechnology, which may nevertheless only represent a very small part of their current product portfolio) are typically in the military (e.g., Raytheon, Lockheed Martin) or IT (e.g., IBM) sectors in the USA. In Europe, chemical companies are very active in the development of nanomaterials (e.g., BASF in Germany). In Japan, engineering, electronics and chemical companies are all actively carrying out nanotechnology research (e.g., Toyota, Toshiba, Mitsubishi).

6. Locating supply partners

Although the nanotechnology research community is very healthy, judging by the tremendous amount of publishing activity (one might even say overhealthy, because there is insufficient coordination, leading to duplicated effort and the neglect of gaps), the same cannot be said of the nanotechnology industry. There are numerous companies offering nanomaterials (overwhelmingly nanoparticles), mostly in the USA and China,[3] but these materials are in no sense standardized and buyers are likely to have to pay a premium price because of the difficulty of comparison no price transparency, hence absence of real competition. A highly significant milestone has been the launching, at the end of 2010, of the Integrated Nano Science and Commodity Exchange (INSCX),[4] which offers trading services in nanomaterials and nanodevices akin to the well established exchanges for commodities such as metals and grains [34]. This exchange is expected to transform the way nanomaterials are sourced. Among other effects, it is likely that the prices of many nanomaterials will fall to a level at which their use can be contemplated (whereas at present, although there may be a clear technical advantage, they are simply too expensive).

Table 3 elaborates the four current business models comprising the nanomaterials supply chain, covering NAL 4–8. By dividing the chain up in this way, the amount of investment needed to take a new material that emerges from a research laboratory (NAL 2–3) to a finished good in the market (NAL 8) is also divided into more attainable parts, especially by a small start-up company. Most nanotechnology start-ups use model A or B, sometimes C (the boundary between B and C is fuzzy): they must rely on finding other companies able to act as customers or partners in order to deliver goods to the marketplace (e.g., Nucryst has partnered with Smith & Nephew). Models C and especially D typically require large quantities of (venture) capital.

It remains an open question whether the nanotechnology industry will follow the consolidation that has occurred in microtechnology—in 1997 there were around 360 organizations worldwide offering to supply technology or prototypes [63], contracting to around 60 by 2001 and 10 or less (counting profitable suppliers only) by 2006. Current the industry has a number of structural weaknesses, making the landscape rather unstable, especially regarding ownership and location of facilities.

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[3]   For example, US Research Nanomaterials, Inc. (http://www.us-nano.com).
[4]   http://inscx.com

Table 3. Business models for the nanomaterials supply chain [63].

Business model label	Description	Examples of products	Examples of companies
A	Nanostructured materials supplier	Nanoparticles, CNT, quantum dots, dendrimers	Thomas Swan, Qinetiq Nanomaterials
B	Formulations and additives	Dispersions, pastes, powders in dispensers	Zyvex (CNT formulations), Oxonica (diesel fuel additives)
C	Enhanced materials	Ready to use polymer composites, coated fabrics, laminates	Nucryst (wound dressings)
D	Finished goods incorporating nanotechnology	Car body panels, clothes, tennis balls, pharmaceuticals	Uniqema (paint)

7. Propellants and explosives

7.1 Rocket propulsion

The traditional approach to making energetic materials is to mix separate oxidizing and fuel substances. The more finely substances are divided, the faster the material will burn; that is, the greater its power density. If $d(t)$ is the nanoparticle diameter, writing $d(t = 0)$ as d_0 we have

$$d(t)^2 = d_0^2 - kt \tag{1}$$

where k is the combustion rate coefficient, typically of the order of 1 mm^2/s. Other beneficial effects of more finely dividing the two substances include diminution of the ignition delay time. Hence, there is a clear benefit in nanification. The ultimate degree of miniaturization might be considered to be a monomolecular energetic material, in which each individual molecule has an oxidizing and fuel moiety. Although the power density is then higher than the mixture, the energy density (total energy released) is typically 10–12 kJ/cm^3, only about half that of a mixture; this limitation might be overcome by polymeric monomacromolecular energetic materials.

A significant practical difficulty that arises with nanified mixtures is dispersion. The extremely high surface:volume ratio of nano-objects (mostly nanoparticles rather than nanorods or nanoplatelets) means that their surface energetic properties play an extremely important role. If the material can be characterized by its three single-substance surface tension components, γ^{LW}, $\gamma^{\ominus}$ and $\gamma^{\oplus}$, corresponding to the Lifshitz–van der Waals (LW) potential, the electron donor potential ($\ominus$) and the electron acceptor potential ($\oplus$), then the interfacial tension (adhesive potential) γ_{12}, where subscript 1 denotes fuel and subscript 2 denotes oxidizer, is the sum of the LW and electron donor–acceptor (da) contributions:

$$\gamma_{12} = \gamma_{12}^{(LW)} + \gamma_{12}^{(da)}. \tag{2}$$

The LW interfacial tension is:

$$\gamma_{12}^{(LW)} = (\sqrt{\gamma_1^{(LW)}} - \sqrt{\gamma_2^{(LW)}})^2 \tag{3}$$

and the da interfacial tension is:

$$\gamma_{12}^{(da)} = 2(\sqrt{\gamma_1^{\ominus}\gamma_1^{\oplus}} + \sqrt{\gamma_2^{\ominus}\gamma_2^{\oplus}} - \sqrt{\gamma_1^{\oplus}\gamma_2^{\ominus}} - \sqrt{\gamma_1^{\ominus}\gamma_2^{\oplus}}). \tag{4}$$

The single-substance surface tension components can be determined from measurements of the advancing contact angles of drops of three different liquids (water, dimethylsulfoxide and α-bromonaphthalene have suitable viscosities) on a flat surface of the material (i.e., fuel or

oxidizer). The experiments are easy to carry out in the sense that no special equipment is required; one simply needs to know how to do them in the right way.

The interaction energy v of the powdered fuel–oxidizer mixture is given by the well known Bragg–Williams expression

$$v = v_{11} + v_{22} - 2v_{12} \tag{5}$$

where the three terms on the right hand side are, respectively, the interaction energies (enthalpies) for fuel particles with themselves, oxidizer particles with themselves, and fuel particles with oxidizer particles. v_{11} and v_{22} are the cohesive energies related to the single-substance surface tensions by the Dupré law

$$v_{11} = -2\gamma_1 A \tag{6}$$

where A is the interfacial area, and v_{12} is the adhesive energy, related to the single-substance surface tensions by

$$v_{12} = -(\gamma_1 + \gamma_2 - \gamma_{12})A . \tag{7}$$

The mixture is miscible (good dispersion) if $v < 0$, and poorly dispersed (immiscible) otherwise. If the interaction energies happen to all be zero, there is still an entropic drive towards mixing.

It is useful to add oxidizable nanoparticles (especially aluminium, also boron) to the fuel in order to enhance its combustion enthalpy. Another possibility is fullerenes [3], C_{60}, C_{70}, C_{76} etc., the diameters of which are of the order of 1 nm.

The smaller these particles, the higher the combustion rate. Furthermore, the smaller the particles, the less severe the erosion of the walls of the system in which the fuel is flowing. This is an example of a situation in which there is an unmitigated advantage in nanification. Moreover, there is no absolute requirement for (expensive) atomic precision in the nanoparticle fabrication; *some* size polydispersity can usually be tolerated.

It should be noted that aluminium readily forms a thin layer of aluminium oxide (alumina) on its surface. It is, therefore, alumina whose surface tension parameters should be inserted into equations such as (4).

Instead of using intimate mixtures of particles (powders), another approach is to create porous sol–gel materials, the gel of which is made from fuel and the pores of which are filled with oxidizer (or vice versa). These kinds of materials have been developed especially by the Lawrence Livermore National Laboratory in the USA.

The ultimate aim of nanotechnology is to perfectly order the components of a structure. In the case of energetic materials comprising separate fuel and oxidizer particles, this can be achieved by perfectly ordering the particles ("nanoblocks"); atom-by-atom assembly is not then required.

One area requiring more research concerns the long-term stability of nano-energetic materials. How will their properties evolve during storage that may last up to 20 years? The enhanced reactivity of finely divided material suggests that degradation will be more rapid than for coarsely divided material.

All the above is at level 2–3. In recent years, the influence of surface-active substances on the particles (Rebinder effect) has been neglected for no particularly good reason, it would appear. Such substances would be especially important for influencing the mechanical sensitivity of explosives. This area of technology is only at level 0 or 1.

7.2 Warheads

Much of the previous Section (7.1) concerning energetic materials is applicable here, except that whereas a propellant should deflagrate, the explosive material in a warhead should detonate. The key question is how nanification affects the deflagration–detonation transition. This still needs to be researched. At present, there is still no definitive theory of energy release mechanisms applicable to real, three-dimensional materials (e.g., the deflagration–detonation transition has been largely studied using model one- and two-dimensional systems; the idea of the highly local-ized hotspot has been highly fruitful but is perhaps still used for want of anything better).

7.2.1 Insensitive energetic materials

It is known that the sensitivity of explosive crystals (such as RDX) can be reduced by improving the crystal quality, diminishing crystal or molecular defects, eliminating voids (pores), eliminating chemical impurities, eliminating multiple phases [61]. The sensitivity depends in a complex fashion on the particle size distribution, the optimization of which is still largely a matter of empirical testing. All of these features point to great potential value of nanotechnology in achieving a new generation of insensitive energetic materials.

The main effect of nanification is to increase the combustion rate (provided the particles are properly dispersed), cf. equation (1). There is, however, another effect due to the enormous increase in surface:volume ratio. The surface molecules have a significantly different coordination environment and, hence, reactivity compared with their bulk congeners. This not only affects the way the fuel reacts with the oxidizer, but may also lead to the surface of either component or both becoming slightly passivated. Provided this can be controlled, it is of interest for conferring insensitivity on munitions (level 0).

At present, the main strategy for achieving relative insensitivity is to cover the energetic material particles with a relatively inert ultrathin coating. If large-scale nanofacture at reasonable cost becomes feasible (but note, this is considered to be in the long-term), rationally designed materials can be assembled atom-by-atom precisely as required (level 1).

7.2.2 Munitions containing nanoparticles

There are some potential health issues arising through the release of nanoparticles in an explosion. This is particularly relevant to the question of collateral damage caused by precision weapons. Nanoparticles are already known to have a great variety of biological effects (see, e.g., [49]), and the subject continues to be intensively researched. There are two main kinds of behaviour: (i) nanoparticles made from a material that is chemically toxic and which is released in the human body through dissolution of the particle; and (ii) insoluble nanoparticles or nanofibres that cannot be destroyed by the body's defence systems and which, therefore, remain as sites of persistent inflammation, with potential adverse secondary effects such as the growth of neoplasm. For category (ii) the surface properties are often decisive in determining the nature of the interaction of a nano-object with its biological, protein-containing environment; hence, an approach based on interfacial tension (cf. Section 7.1) can be used to predict such interaction.

7.2.3 Switchable explosivity

As mentioned (Section 7.2.1), the present strategy for creating insensitive explosives is to mitigate ignition sensitivity by placing appropriately inert coatings around the particles of explosive material. It might be thought that in view of the fact that the theory of explosions is itself still in a fairly rudimentary state (indeed, the current "hotspot" notion might well be superseded in due course), it is presently difficult to rationally design an explosive with switchable sensitivity. However, this particular problem might not require a profound understanding the nature of explosions: it might well suffice to consider how the degree of ignition mitigation of a coating can be altered by an external environmental parameter, which appears to be a considerably easier problem and one for which a solution might well be achievable in the medium term.

Switchable sensitivity would be useful to enable a fuse to be insensitive until activated close to anticipated demand. Nanotechnology is expected to facilitate the achievement of this property through atomic-detail understanding of the overall process.

8. Applications involving electricity (including electronics)

8.1 General challenges

In any modern complex weapon, information acquisition and processing plays a crucial role.[5] Unlike several decades ago, when military applications drove advances in information processing electronics, nowadays such applications only represent a fraction of a percent of global turnover, which is dominated by consumer applications, mainly computer games. The chips that drive them are generally powerful enough to serve almost any movable application, and the militarization of this civilian technology does not present any great technical problem.

Three general areas, however, are of such great importance for missiles that specifically targeted development work seems to be warranted. These are heat management, energy storage and power conduction. Heat is especially undesirable in a missile because of the possibility of unwanted ignition of fuel or warhead. Increasing both specific energy and energy density of energy storage are of importance because of the continuous downward pressure on space and weight in a missile, whose objective is to deliver a warhead to a particular location; the warhead should comprise the greatest possible fraction of total missile space and weight. Smaller electrical batteries will allow a larger warhead to be carried (or a reduction in size and cost of the rest of the missile, if the warhead is already appropriately sized). A similar consideration applies to electrical power conduction. Current technology uses copper. The weight of the cabling is such that a second battery might be preferable to connecting a central one to a distant location.

8.2 Heat management

Heat management has grown in importance with the nanification of electronics, because the concomitant increase in the number of components per unit chip area implies a parallel increase in the heat generated per unit area.

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[5]   In the V2, dating from the early 1940s, the instrument compartment comprised about 12% of the total net weight of the rocket [55].

8.2.1 Nanofluids

Nanofluids are defined as suspensions of nano-objects (e.g., particles) in a liquid; in other words they are a kind of liquid composite. Currently, the most important purpose of the added nanoparticles is to increase the thermal capacity of the liquid. A potentially problematical aspect is the agglomeration or even aggregation of the nanoparticles, which will lead to their removal from circulation and, hence, progressive degradation of the thermal properties of the fluid. While they are still circulating in partially aggregated form, as larger objects they will lead to enhanced erosion. Careful control of the surface properties is, therefore, necessary. Adapting the surface tension formalism already introduced in Section 7.2, we need to ensure that the nano-object–liquid interfacial free energy has a positive sign.

Some nanofluids are already available commercially (e.g., CuO in water). Substitution for pure cooling liquids may be attended by problems due to the not insignificant viscosity changes, among other things (e.g., [42]), but one can probably consider this technology to be already at level 4.

8.2.2 Thermal interface materials

Since the surface of the object emitting heat inevitably has a certain roughness, its contact with any juxtaposed heat sink will be imperfect. As in tribology, only the contact asperity is relevant, and its area may be quite small. The purpose of thermal management materials is to fill the gaps. These materials are typically pastes of highly conducting nano-objects (carbon nanotubes are especially useful—cf. Table 6— dispersed in silicone grease (e.g., [57]). A 10% volume fraction of the nano-object filler can increase the thermal conductivity of the material from about 0.2 W/mK to almost 2 W/mK. Their use as thermal interface materials (TIM) can typically diminish the interfacial thermal resistance by an order of magnitude (around 5 mm^2 K/W is achievable). TIMs are essentially a kind of nanofluid that is preferably solid when cold. They have already attained level 4–5.

8.2.3 Carbon nanotube arrays

This concept exploits the extremely high thermal conductivity of carbon nanotubes (cf. Table 6). They are synthesized directly on the silicon or silica substrate and perpendicular to it, forming a very efficient bridge between the electronic component and the heat sink [64, 54] (level 1–2).

8.3 Electrical cabling

Carbon nanotubes (CNT), novel nano-objects that have no bulk equivalent [9], have, in certain forms, remarkable electrical attributes (Table 4). In the so-called "armchair" structure (in which the chiral vectors are equal) the band structure is metallic and the current capacity of the nanotubes is several orders of magnitude greater than that of copper (Table 4), in contrast to nanotubes having the so-called "zigzag" structure, which are semiconducting. The difficulty in creating a macroscopic electrical current-carrying cable, whose mass per unit length would be far smaller than that of an equivalent copper cable, is essentially one of assembling and connecting up the nanotubes to make a macroscopic conductor. A single nanotube has a diameter of the order of 1 nm. Until relatively recently they could only be manipulated individually using the laborious procedures associated with scanning probe ultramicroscopies. An early approach

was to randomly disperse them in a polymer matrix [38, 65, 15]. Because of their extreme elongation, the percolation threshold is rather low (typically much less than 1 vol-%) but these composite materials had disappointingly low conductivities (Table 4), presumably because each nanotube may only contact other nanotubes at two points and the contact resistance is high. Some improvement was noted when the nanotubes were clustered [4]. A significant breakthrough occurred with the demonstration of the ability to spin nanotubes into a yarn [66]. In such a material each nanotube may make hundreds or thousands of contacts with other nanotubes and the overall conductivity is correspondingly higher (Table 4). A single strand of yarn may have a diameter of some micrometres, and such strands may be braided or woven to create even larger structures [10].

Table 4. Some electrical properties of graphite and metallic carbon nanotubes,[a] compared with metals.

Property	unit	graphite[b]	CNT	composite	yarn	Cu	Al
Resistivity	Ω cm	0.1	$5 \times 10^{-6\,c}$	$> 100^{\,g}$	$10^{-5\,d}$	1.7×10^{-6}	2.7×10^{-6}
Current capacity	A cm^{-2}	20	$2 \times 10^{7\,d}$	?	$3 \times 10^{4\,d}$	$600^{\,h}$	$350^{\,h}$
Density	g cm^{-3}	2.1	$2.5^{\,f}$	1	0.8	8.9	2.7

[a] The given values are only approximate. Actual measured values still depend on many experimental details.
[b] Typically in the form of a carbon electrode.
[c] [16]. [d] [53]. [e] [68]. [f] Multiwalled.
[g] The range of values is large. The polymer matrix without the nanotubes would typically have a resistivity of the order of 10^{17}.
[h] This is not very precisely defined, typically by when some destruction of the cable or its insulation takes place.

Various improvements in the spinning process have been reported. For example, spinning from a dispersion of single-walled carbon nanotubes (SWNT) to which surfactant had been added resulted in a resistivity of $2.8 \times 10^{-3}\,\Omega$ cm [33]. Even more dramatic improvements were achieved by doping carbon nanotubes (double-walled) with iodine, enabling resistivities of as low as $10^{-5}\,\Omega$ cm to be reached [68].

Another difficulty in realizing CNT-based cabling is the fact that known synthetic procedures for making the nanotubes produce a mixture of semiconducting and metallic ones, and of single-walled and multiwalled. One way of overcoming the problem is to refine the synthesis parameters [41]. Methods of purifying the mixture are also being devised, including centrifugation [21] and affinity separation using DNA [59, 60].

8.4 Power storage

8.4.1 Electrical storage devices

Electrical capacity depends on the distance separating the oppositely charged plates in a condenser, and interfacial area contributes to the performance of chemically-fuelled storage batteries. It is obvious that such systems can be structurally enhanced with respect to performance by nanification. A great deal of work is currently being undertaken in many

laboratories worldwide (but especially in the USA, Japan and some European countries) on these topics, and on the related one of hydrogen storage. The feasibility of implementing any technically appropriate solution will depend on issues such as compatibility and total lifecycle. Previously, it has been accepted that the relatively small achievable improvements in, say, supercapacitor performance through replacing carbon black, which is a very imperfect nanomaterial, by precisely fabricated carbon nanotubes were not worth the great increase in expense. However, improvements in carbon nanotube synthesis are constantly taking place and the feasibility of any proposed application will need to be assessed in terms of the very latest technology developments.

Table 5 compares the specific energies and energy densities of some current and emerging technologies. A third parameter is specific power ("gravimetric power density"). Here, capacitors are as good as combustion fuels (around 1 MW/kg), which are much better than batteries and fuel cells (around 100 W/kg).

Table 5. Specific energies $\mathcal{E}$ and energy densities $\mathcal{D}$ of existing storage systems,[a] ranked by $\mathcal{E}$.

Type	$\mathcal{E}$/MJ kg^{-1}	$\mathcal{D}$/GJ m^{-3}
Gasoline[b]	46	34
Aluminium[b]	31	84
Al-air battery	4.6	?
Thermite	4	18
Fuel cell[c]	1	wide range
Li-ion battery[c]	0.7	2
Na-NiCl battery[c]	0.43	?
Lead-acid battery[c]	0.14	0.36
Supercapacitor[c]	0.1	0.2

[a] Specific energy is energy per unit mass—sometimes, confusingly, called energy density, which is energy per unit volume. The latter are less well defined than the former and are liable to increase as new (nano)materials are developed.

[b] Not self-contained—requires external oxidizer and a combustion apparatus, the effective (practical) output from which might only be 10% of the given figure.

[c] Approximate, from laboratory experiments (there is a wide range depending on design and other considerations).

It will be noted that the Al-air battery (a rechargeable device developed by Europositron) comes close to the practical output from the gasoline-fuelled internal combustion engine. The best fuel cells are still operating far below their theoretical limits, but given that the field has already been researched for about 170 years it must be conceded that the barriers to further progress are considerable. Nanotechnology can in principle contribute in many ways. Lightweight refractory nanocomposites could increase the effective specific energy of gasoline, and nano-engineered catalysts would benefit fuel cells. Nano-engineering will have the most direct impact on supercapacitors, whose stored energy depends directly on their internal surface area. Some of these nanotechnologies are already at level 5.

A bald list of specific energies might not be adequate to convey the potential of the technologies. Very often it is through judicious combinations that really important benefits can be achieved. As an example, consider remote equipment such as miniature sensors needing small amounts of electrical power round-the-clock. The combination of a small photovoltaic solar cell

together with a supercapacitor capable of storing surplus energy during the day and releasing it at night allows the equipment to be completely autonomous regarding its energy requirements. This is the current state-of-the-art.

Supercapacitors are still undergoing intense development (already at level 4). Rather than relying on random nanostructures (e.g., carbon black) *regular arrays* of nanofeatures may offer an increase of one to two orders of magnitude. This would put supercapacitors ahead of the experimental Al-air battery and the practical output from gasoline. An intermediate, semistructured development is to incorporate carbon nanotubes into cellulose-based paper [43]. Hitherto the main exploitation of nanotechnology for capacitors has been to increase the plate area. Nanoscale plate separation limits the voltage that can be stored on the plates because of arcing. There are now attempts to examine the theory more deeply, taking quantum effects explicitly into account, in order to understand how capacitor plates with separation distances in the nanoscale could be designed to avoid arcing at high voltages.

Obviously specific energies can only be compared if all other things are equal. These "other things" include all the infrastructure required to sustain the chosen system, including its cost, as well as charge/discharge characteristics, lifetime etc. At least there seems to be no shortage of lithium as a raw material. Apart from efforts to increase power and energy densities, increasing the rapidity of charging and discharging would also be useful. Here too, regular nanostructures might be the key. Some of the technologies, notably fuel cells, have been hampered by large minimum practicable sizes. Here again, micro- and nanotechnologies may be helpful (e.g., see [25] for an example concerning fuel cells).

The novel nanomaterial graphene is currently being explored for a variety of energy storage applications. Clearly it is a candidate for capacitor plates, provided it can be stably configured. Carbon nanotubes are also finding novel applications, notably as high-capacity anodes in lithium ion batteries. A more exotic application is as a scaffold for fuel coatings which, when ignited, create a thermal (combustion) wave or thermowave that entrains electrons as it moves along the carbon nanotube, generating current.

Apart from the above technologies, there is also design work being done on improving the nanoscale integration of the disparate components of electrical storage media. Miniature nuclear batteries incorporating radioisotopes are being explored, but are microscale rather than the nanoscale and hence out of scope. Also not, strictly speaking, nanoscale is the novel organic radical battery developed by Prof. Hiroyuki Nishide at Waseda University (Tokyo) [40]. It consists of stable n-type and p-type radical polymers separated by an electrolyte, and should achieve both the high specific energy densities of secondary batteries and the high specific power densities of capacitors. A notable advantage is the rapidity with which it may be recharged.

8.4.2 Hydrogen storage

Conventional hydrogen storage is either as a gas in a high pressure cylinder or as a liquid at low temperature. For example, at 200 bar the volumetric density is approximately 10^{22} H-atoms/cm^3. In its liquid state (at 20 K) the density is fourfold that figure, and fivefold as a solid at 4 K. These figures exclude the sizes of the pressure vessel and the cryogenic equipment, the masses of which make it difficult to compute the gravimetric densities. Similar ambiguity attends the comparison of specific energies. Remarkably high densities can be achieved by storing the hydrogen in a

metal as its hydride. For example, MgH_2 contains 6.5×10^{22} H-atoms/cm^3, although the fraction of the total mass that is hydrogen (i.e., gravimetric density) is only 0.076 (compared with about 0.04 for a high-pressure container). The main challenge in hydrogen storage is considered to be how to increase this mass fraction. High storage capacity is not, of course, the sole criterion; other operational parameters such as charging and discharging rates, how much energy is required for charging (usually by high pressure) and discharging (usually by elevated temperature) and how many times it can be done before the structure deteriorates (the US Department of Energy specifies 1000 cycles) are also important. Many metals and alloys (typically of the general formulae AB_2 and AB_5) have been investigated. These have the advantages of operational pressures and temperatures within the practical ranges of 1–10 bar and 0–100 °C, unlike the more primitive substances such as MgH_2. $LaNi_5$ and its derivatives look very promising; hydrogen density at 2 bar, while not as good as that of MgH_2, equals that of gaseous molecular hydrogen at 1800 bar (this density is reduced by the packing fraction if the alloy is in powder form); adsorption is fast and reversible; cycling life is good. However, the achievable densities, even of MgH_2, are not as good as that of gasoline, which contains about 7×10^{22} H-atoms/cm^3. A variety of more exotic compounds, capable of releasing hydrogen in the presence of a catalyst (e.g., formic acid) are being studied, but none are being seriously developed at present. An interesting new development has been the "chemical hydrides", such as the Li-B-H and Li-N-H systems. Compared with the heavy metal alloys, these light elements yield much better hydrogen mass fractions (0.18 for $LiBH_4$). Most of this technology is chemistry. More relevant to nanotechnology is the possibility of using graphene or carbon nanotubes to store hydrogen, or even relatively ill-characterized activated carbons. The achievable hydrogen storage (gravimetric) densities are, however, rather on the low side (~ 0.04). Physisorption seems to be the mechanism of adsorption, a corollary of which is that rather low temperatures suffice to get a reasonable amount of desorption.

In summary, hydrogen storage is a very active academic research field and the accumulated literature is already enormous. Little attention seems, however, to be paid to the practicality of large-scale deployment of some of the more exotic materials. Reports summarizing new materials typically do not compare all relevant parameters, which include charging and discharging rates and energies apart from the overall storage capacity. The field is heavily driven by the automotive industry, the major players in which are carrying out intensive research. Presumably any military application would be based on what was available from that sector. The purpose of the stored hydrogen would be—presumably—to supply fuel cells used to generate electricity.

As mentioned, the field is dominated by chemistry. The results obtained from exotic, highly structured materials (such as organosilicas) hint that rational nanomaterials design and assembly could yield storage materials with very attractive properties, although they could not at present be manufactured in the necessary large quantities. From that viewpoint, low-cost ways of making hierarchical porous materials based on well established industrial processes (e.g., weaving electrospun polymers into sheets) seem to be rather attractive (level 2–3), with performance comparable to that of carbon nanotubes.

In general, nanification of the material (e.g., by having it in the form of nanoparticles, or by loading it into an aerogel of some inert material) will benefit the kinetics of charge and discharge,

but typically will also result in less extreme environmental conditions (temperature and pressure) being required (e.g., [62]).

The most exciting trends are those in which hydrogen responsivity is built into a material, such as the "pore-with-gate" metal organic frameworks being developed at the University of Nottingham. This type of approach is still very much in its infancy (level 0–1).

8.5 "Hardening" electronics

In the medium term, there is interest in "hardening" information processing systems, meaning making devices resistant to extreme environments, including high levels of radiation or extreme temperatures. There are two ways of achieving this. The first is through mechanical logic devices. Miniaturizing electromechanical devices such as the familiar relay down to the nanoscale is very attractive because the resonant frequency ω_0 of the vibration of a cantilever is given by

$$\omega_0 = \sqrt{k}\,/\,m \sim 1\,/\,l \tag{8}$$

where k is its spring constant (stiffness), m its mass and l its characteristic linear dimension. Hence nanoscale mechanical devices can respond extremely quickly. Furthermore, the minute size allows whole arrays to be placed in a controlled environment (e.g., vacuum) ensuring a low friction coefficient and, hence, an extremely high figure of merit (quality factor). In consequence we might well see a resurgence of mechanical computing devices, particularly exploiting the extraordinary stiffness of carbon nanotubes [8]. This area is at level 1.

The second way is to create a complete set of conventional electronic components using the new nanoscale carbon materials as components instead of silicon and associated elements (perhaps already at level 2).

In the longer term, three new areas of development are anticipated. By "longer term" it is meant that the developments cannot be thought of as an extrapolation of the trends that have hitherto ruled the field, which are exhaustively covered in the International Technology Roadmap for Semiconductors (ITRS). The current (2009) edition of the ITRS covers developments up to 2025. "Longer term" is, therefore, deemed to refer to after that.

The first new area is denoted spintronics. In its "soft" form it refers to the influence of electron spin on electron conductance, already discussed by Mott in 1936. This phenomenon is now being exploited commercially in the readers of magnetic storage media, making use of the giant magnetoresistance effect or based on the magnetic tunnel junction. These spintronic devices offer extremely high sensitivity to magnetic fields. The next development is to gate electrons in transistors by controlling their spin. Experimental devices have been constructed from stacked nanoplates, but it is not clear what the overall benefit would be (level 1–2).

A more radical development ("hard" spintronics) is to replace electron charge (i.e., the presence—or absence—of an electron) as the carrier of information by electron spin. Logic gates can be constructed using single spin logic (SSL) [7]. This has the enormous advantage that the electrons do not need to physically move. Movement is inevitably associated with power dissipation ($\propto I^2R$), except in devices so small that the electrons move ballistically—but there is doubt as to whether such devices could ever be manufactured on a large scale. Indeed, managing the heat generated by conventional electronics is one of the major challenges (cf. Section 8.2).

In SSL, electron currents do not flow. SSL devices would presumably be realized using arrays of quantum dots, but at present the concept is more theoretical than practical (level 0). Apart from conceptualizing SSL, current research focuses on increasing the quantity of spins available for operations.

The second new area is quantum computation. This is not specifically linked to nanotechnology, except that the smaller a device, the easier it is to isolate it from its environment, a necessary condition for quantum computation. This development can be expected to occur on the same (long) time scale as assembler-based nanomanufacture and need not be further considered in this review.

The third new area seems to be more promising than quantum computation, in the sense that there seem to be fewer barriers to its practical realization. This area exploits the exotic current–voltage characteristics of nanostructured materials, which means using them to generate novel information processing architectures (e.g., [52]), a field which actually began by considering the characteristics of biological systems. For example, the bilayer lipid membrane, ubiquitous in biology, can host many exotic molecules that may confer giant inductance and other interesting memory effects such as memristance on it (e.g., [18]). Much still needs to be researched, the main limitation being the very small number of experts in the field, which definitely lies outside mainstream effort.

9. Optics

The natural length scale of any optical system is given by the wavelength of the radiation. At first sight, this implies that only far-ultraviolet (UV) radiation and X-rays can possibly benefit from nanotechnology. Certainly, there are new technologies interesting for imaging and so forth (i.e., working in the visible or near infrared range of wavelength), such as microlens arrays, that are definitely in the microscale and hence excluded from this review. Subwavelength structures are, likewise, in the microscale and typically achieved by precision machining; although they could in principle be achieved by the programmable self-assembly of nanoblocks there appears to be no work currently being carried out in this direction. Some thin film (e.g., antireflectance) coatings applied to optical surfaces are, technically, nanoplates but their behaviour is well understood using classical optics and, hence, these are also excluded from this review. Some coatings are, however, mentioned in Section 9.4.

9.1 Infrared detection

The challenges of infrared detection are well known: sensitivity (including maintaining a special environment for the detector) and cost. They are complementary; the two extremes are well represented by mass-produced pyroelectric sensors suitable for use in low-cost applications such as person-sensitive corridor lighting, but having severely limited responsivity, and military night vision sensors operating at cryogenic temperatures, which are very sensitive but bulky and expensive. Technically, these two approaches to detect infrared radiation are "thermal" (the radiation heats the detector element, changing some physical property of the material) and "quantum" (individual infrared photons falling on the detector are counted).

Pyroelectric materials are attractive for thermal detectors. The temperature change alters the polarization of the material, which is typically arranged in an array, the lateral dimensions of the

elements of which might well be in the nanoscale and its thickness almost certainly will be. Alternatively, the change of resistance of the material with temperature might be monitored.

A different approach is to create a cantilever out of two materials of different thermal capacities; heating it will cause it to bend and the bending can be detected (e.g., by monitoring the displacement of a beam of light reflected from the cantilever). Microsystems technology can routinely make such structures in the microscale, and this capability has now been further miniaturized down to the nanoscale in research laboratories.

The quantum detectors work in the same way as visible light photodiodes, but the small energy of infrared photons requires cryogenic temperatures to reduce the noise. Alternatively, severe reduction of dimensionality of the narrow band gap semiconducting material used to create the photodiode—for example, creating zero-dimensional quantum dots, makes an intrinsically low noise device. Carbon nanotubes, in their semiconducting form, are also attractive candidates and represent the first true nanoscale infrared detector. Such devices are being investigated in several academic laboratories (level 1). The leading institution appears to be Michigan State University. The preferred configuration is to place a single nanotube across the gap between two electrodes. The electrodes are made by standard semiconductor processing technology. A drop of a suspension of the nanotubes in a liquid is then placed on the gap and an AC signal applied across the (gold) electrodes to create a highly nonuniform electric field, which eliminates all but a few nanotubes by dielectrophoresis. The final selection of a single nanotube requires nanomanipulation (e.g., using an atomic force microscope). The resistance of the nanotube falls significantly under infrared illumination [12].

9.2 Metamaterials

The construction of metamaterials is dependent on the deep modern insight into the optical properties of materials that initially came from V.G. Veselago [24]. Thus, it is possible to construct a material with a negative refractive index and this has already been done, famously, by Shelby et al. in 2001 with microwaves, and more recently for visible light [29]. These metamaterials are periodically distributed metal resonators with negative electric conductivity and magnetic permeability. Standard semiconductor processing technology can be used to generate structuring down to a few tens of nanometres in size. It is this capability that has recently enabled metamaterials working at visible wavelengths to be constructed.

An object coated with such material would be invisible over a limited spectral width. In order to make large objects in invisible over the entire visible or radar spectrum, so much more needs to be done that this development really belongs to the long-term category (level 1).

If the capability of assembling exotic materials through assembler-based atom-by-atom placement is developed, materials combining desirable optical and other properties might become feasible. For example, mechanically strong materials that transmit infrared radiation would be very useful as sensor windows in missiles. Such custom optics (designer materials) are not yet, however, a reality. More fundamental knowledge of the structure–function relationships of materials is required.

9.3 Switchable optical materials

By "switchable" it is meant that some change in the external environment engenders a significant change in one or more attributes of the object, which may typically be a coating, a thin plate, or a fully three-dimensional bulk material. The application nearest to implementation is switchable reflectance. Indeed, materials with switchable optical properties such as photochromic glass (containing silver halide nanoparticles) have been invented some time ago. For certain applications, such as controlling the amount of sunlight traversing a window into an interior room, the technology is suitable but one should note the slow response time, the high cost and the lack of data on the long-term stability of the material. A large number of electrochromic materials are known—they have been extensively developed for the commercial display of alphanumeric and other kinds of data produced by computing devices. However, these materials (typically organic liquid crystals, e.g. [50]) are mostly too fragile to be exposed to an open environment and are expensive enough to preclude their large-scale application (e.g., to the fuselage of an aircraft). Besides, it might be very awkward or completely impracticable to set up appropriate electrodes to provide the necessary electric fields. In such circumstances, materials that can be switched from one reflecting state to another by an external attribute such as the presence of a certain gas or simply temperature, might be more attractive—provided that one has proper control over the external attribute. Vanadium dioxide has become popular as a model of dramatic temperature-dependent reflectance change due to the change from a semiconducting (at low temperature) to a metallic (high temperature) form [31]. Typically the VO_2 is present as nanoparticles in a silica matrix, and the composite can be applied cheaply over large surfaces by spray-painting a slurry. Another set of materials having a metal–semiconducting (or insulating) transition are rare earth and transition metals that change their reflectance according to their degree of hydrogenation. Some of these materials are available commercially in the form of switchable mirrors. Given that this field is already being quite actively investigated (level 2–4), depending on specifications a suitable material might already be known, which would merely require development of, say, an appropriate method of applying it where required.

Switchability is ubiquitous in nature and one should not overlook the potential of biomimetic switching, especially if the principles of the mimicry can be applied to nonbiological, wholly inorganic materials. The ever-increasing sophistication of structural biological methods are constantly yielding fresh insight into how switching of attributes takes place in living organisms (e.g., the silk proteins that are the precursors of spider webs are switched between a compact storage form and an assembly form [20]). Equally fascinating is the mechanism of environmental adaptation of the skin of chameleons and other creatures such as the octopus. It is not understood in fine detail, but it is known that it is a cell-based mechanism. Apparently, beneath a transparent outer skin there are specialized cells containing pigment granules (i.e., nanoparticles). If the granules are concentrated in one small zone the cell is essentially transparent. If, on the other hand, they are dispersed throughout the cell, the granules will pigment the cell. It is not currently understood how the cells can relocate their pigments so rapidly (level 0).

9.4 Other coatings

There is scope for improving the performance of imaging systems by enhancing the resistance of their outermost components (i.e., lenses or windows) to adverse environmental influences: antidust and antifog properties in dusty and humid conditions, respectively. In the former case the surface properties of the dust (e.g., silica-based in the Sahara Desert) need to be well understood. Armed with adequate knowledge of the environmental contaminant, one can then proceed to design a suitably repellent surface (cf. the interfacial energetics discussed in Section 11). According to the well known Cassie–Wenzel law [56], the repellency can be enhanced by nanostructuring, which is, advantageously, accomplished at two or more different length scales [48].

10. Materials

This section covers materials that cannot be assigned to electronics or optics.

10.1 Electrorheological fluids

Electrorheological (ER) fluids are materials whose rheological characteristics are controllable through the application of an electric field. For example, they can be switched from a freely flowing liquid to a rigid solid. They consist of a suspension of nanoparticles in a liquid. The simplest type is called a dielectric electrorheological (DER) fluid: the material components (nanoparticles and liquid) give a linear electrostatic response [32]. The nanoparticles should have a conductive core and an insulating shell. A simple explanation of their mechanism is as follows. Consider two conducting spheres of radius r separated by a small distance δ between their surfaces, suspended in a liquid of dielectric constant ϵ. If $r \gg \delta$, the mutual capacitance C is proportional to $r \ln r/\delta$. Now apply an electric field E along the axis joining the centres of the two spheres; the free energy density is proportional to C. Now apply a shear perpendicular to the electric field. The line segment joining the two centres will be lengthened to d and tilted by an angle θ. We have $(2r+d)\cos\theta = 2r+\delta$, which gives $d \approx \delta + r\theta^2$ for small angles. The shear stress is $(\partial C/\partial\theta)/R$, which is proportional to $(r/\delta)\sqrt{(d-\delta)/r}$. This has a peak value at $d = 2\delta$, which defines the static yield stress. It is approximately equal to $\sqrt{r/\delta}\epsilon E^2/(8\pi)$. This simplified derivation provides important clues for maximizing the electrorheological effect; that is, producing the greatest yield stress for the least applied electric field.

These ER fluids are only experimental materials at present, mainly developed by the Hong Kong University of Science and Technology. It is unnecessary for the core to be a solid conductor; to reduce the mass of the individual particles it suffices if the core is made from some cheap, lightweight material (e.g., silica glass) coated by a thin metallic layer, in turn coated by the insulating layer that can also usefully provide wear resistance (level 2–3).

10.2 Smart frangible missile covers

Munitions such as missiles and rockets are typically launched from canisters, which provide environmental protection prior to launch. Environmental factors against which protection is provided include humidity and water, extremes of temperature (including icing), hail, debris impact from transportation, debris impact from the launch of adjacent munitions, acoustic noise,

electromagnetic interference, and nuclear, biological and chemical contaminants (including corrosion-inducing substances) as well as substances used to counter these contaminants in decontamination operations. After launch the canister will typically be discarded.

The munition departs from one end of the canister, which must either be opened immediately prior to launch, or be broken by the passage of the munition through it. Mechanical opening is clearly expensive and would require additional power and regular testing. Hence, canisters are typically closed using a cover that is ruptured due to launch pressure or the forward motion of the munition. The types of cover are:

1. A thin membrane that is punctured
2. A hard material that is fractured
3. A solid foam (a brittle, interconnected network) that is fractured.

All these types have disadvantages. 1 and 3 are not very durable, and offer limited environmental protection. 2 may fracture into irregular fragments, some large enough to damage the munition and any persons in the vicinity. One way to mitigate the uncontrolled fragmentation is to heat-treat glass (the same process used to create automobile windscreens that shatter into small cubes a few millimetres in size when subjected to stress). However, although the fragments are rather uniform they are still large enough to potentially damage a fast-moving munition. An ideal material would fragment into nanosized pieces.

Apart from controlling fragment size, a main difficulty is to sufficiently separate the maximum energy that can be applied without causing fragmentation and the minimum energy that must be applied to necessarily produce fragmentation. This energy gap is required to prevent accidental fragmentation.

10.2.1 Frangibility and "smart" frangibility

Frangibility is the capability of being broken; that is, the opposite of toughness. All materials are frangible if subjected to a sufficiently strong force. As mentioned in the previous section, there should be an energy gap between the maximum energy that can be resisted without fragmentation and the minimum energy required to initiate fragmentation. Alternatively, if fragmentation results from releasing stored energy, there must be an energy barrier preventing spontaneous or otherwise unwanted release.

Smart frangibility means that the material will behave correctly (that is, break up into fragments) whenever required under a range of possible ambient conditions. This could include a broad range of temperature and humidity. A more restricted performance is that of "responsive frangibility", in which the material will break up in response to an external stimulus, but the nature of the stimulus will be narrowly defined.

Provided fragmentation is sufficiently rapid, it can be triggered by the tip of the nose cone of the missile touching it, which can always be assumed to have enough energy. Hence, it is not necessary to have an external electrical, magnetic or optical field for triggering.

10.2.2 Existing approaches to the problem

Apart from the membranous, hard or foamy missile canister covers mentioned above, composite frangible materials have been quite extensively investigated for anti-ricochet projectiles and

bullets for soft targets. The two principal approaches to create them are:

1. Mix and sinter a variety of metal powders, or metal and ceramic powders;
2. Embed metal powders in a polymer matrix.

The (adhesive) bonds between the components require significantly less work to rupture than the cohesive ones holding the component objects internally together. Of particular interest is the work of Abrams et al. of Delta Frangible Ammunition (Stafford, Virginia), who investigated the effectiveness of certain additives (silica, alumina, molybdena, molybdenum sulfide and graphite) on the frangibility of composite materials whose metal was copper powder [1]. Silica increased the frangibility but alumina and molybdena diminished it. Graphite had little effect, and molybdenum sulfide also diminished the frangibility. Limited as these results are, they do represent somewhat more knowledge than is contained in the numerous other patents on frangible bullets.

Some work has been done in designing special shapes, rather than just using spheres or randomly irregular shapes, in order to improve the fragmentation parameters.

The chemical industry (e.g., W.R. Grace & Co.) has taken an interest in frangible materials as catalyst supports [14]. These are essentially silica-based aerogels. An attrition quality index (AQI$_x$), defined as the difference in the (weight) percentages of particles below a certain size x before and after stress, characterizes frangibility.

10.2.3 The theory of frangible materials

Fragmentation of a material occurs because of the rapid propagation of cracks (fractures). Composite materials experience local stresses, which separate the main component from the binder. Another type of material is based on carefully balancing compressive and tensile stresses. This is known as toughened or tempered glass, which is basically made by rapidly cooling molten glass. Since the surface layers cool and contract more rapidly than the core, they solidify in compressive stress, after which the core solidifies in tensile stress. The same effect can be achieved by replacing small ions (such as sodium) by large ones (such as caesium) in the surface layers. The final stiffness is essentially the same as that of ordinary annealed glass, but even a fairly small disturbance (e.g., a scratch) can cause the entire material to fragment into small particles; this can be understood according to Griffiths' theory of catastrophic crack propagation. A most remarkable example of this kind of material, which stores potential energy, is "Prince Rupert's drops", made by dropping molten glass into cold water. The heads are extremely tough, but because of their minute size the tails can easily be broken by hand, exposing the cores, from which the crack front propagates at a velocity of hundreds of metres per second, shattering the entire object.

10.2.4 Possible new approaches

1. Investigate composite materials made from metal powder mixed with a small fraction of ceramic (used in frangible bullets). This kind of material seems attractive for use in missile covers because the fragment size is that of the metal powder particles and can therefore be made small enough to do no damage to the emerging missile. There are many choices for the metal and for the binder and the adhesive and cohesive forces can be appropriately chosen.

2. Investigate materials with stored energy made in unusual geometric forms. For example, toughened glass with a forest of thin protrusions on the side facing the missile would catastrophically fragment into dust upon being touched by the tip of the missile nose cone.

10.3 Lubricants

Low-friction coatings are classically made from layered materials such as graphite (C), molybdenum disulfide (MoS_2) or tungsten disulfide (WS_2). As well as the transition metal dichalcogenides, bismuth selenide (Bi_2Se_3) and telluride and boron nitride (BN) are also important, and some transition metal oxides (e.g., MoO_3 and see [27] for a variety of other compounds). Physical vapour deposition (e.g., sputtering) is suitable for applying the coatings. Coating thicknesses are typically several micrometres, and are not therefore in the nanoscale. The layered sulfides can yield a friction coefficient of less than 0.05 (0.005 appears to be possible), depending on environmental conditions (including humidity). This compares with steel on steel, which has a friction coefficient of about 0.8, falling to about 0.1 when lubricated with motor oil. Wear is also an issue, which is probably why thicknesses of less than a few hundred nanometres are not recommended. Some of these materials do not perform well over a wide range of temperature, especially in air, in which oxidation of the non-oxide materials might become problematical at higher temperatures.

Composite films can be used to combine properties. For example, cosputtering gold and molybdenum sulfide creates a low-friction electrically conducting coating useful for sliding electrical contacts [30]. More sophisticated composites are designed to adapt their structure and surface composition in order to maintain their tribological properties under varying conditions. For example, silver and molybdenum nanoparticles in an yttrium-stabilized zirconium oxide matrix, produced by cosputtering, provide a silver-rich surface for low friction at temperatures up to 500 °C, above which diffusion causes the surface to become enriched in MoO_3; the diffusion can be controlled by incorporating a porous TiN layer within the structure [37]. The long-term behaviour of these materials under storage is unknown; at low temperatures (i.e., after fabrication) the structure is metastable.

A successful low-friction coating might make the use of a liquid lubricant superfluous (which is anyway likely to be problematical in electrical applications).

As an alternative to precoating surfaces, the materials can be added to the lubricant in the form of nano-objects (e.g., nanoplatelets, which can be made from a wide variety of tribologically advantageous materials [13]) to lubricating fluids. The observed effects (which may include wear reduction [22]) depend on the deposition of the nano-objects on the moving surfaces.

A very hard carbon film called "near-frictionless carbon" (NFC), better than diamond-like carbon, has been developed by the Argonne National Laboratory; it combines low friction (achieving a friction coefficient of about 0.04 in air and as little as 0.001 in dry argon) with great hardness. Hence, wear rates are extremely low ($< 10^{-10}$ mm^3 N^{-1} m^{-1}, compared with 10^{-3} mm^3 N^{-1} m^{-1} for unlubricated steel and 10^{-8} mm^3 N^{-1} m^{-1} for conventionally lubricated steel).

10.4 Other bulk composites

It is well established that the properties (e.g., toughness) of a matrix (metal or polymer) can be enhanced by incorporating nano-objects in the matrix (reviewed in [58]). Typical enhancements are in the range of tens to hundreds of percent. This allows the creation of structural materials having the strength of steel but much lower density. A drawback, which has hitherto prevented their application in many engineering applications, such as aircraft, is that the long-term fatigue behaviour in service is unsatisfactory or unknown. Missiles have the advantage that they are "single shot" applications and long-term fatigue is not an issue.

Critical issues in composites are dispersion (which is, however, a wetting phenomenon, the science of which is well established, cf. Section 7.1) and, in many cases, positioning (i.e., structuring). Manufacturing conditions for the creation of nanocomposites are far from eutactic and generally the best that can be hoped for is that the added nanocomponents are well but randomly dispersed in the matrix.

10.5 Novel carbon-based nanomaterials

Some of the most interesting new materials are based on blending carbon nanotubes (CNT) or graphene platelets into polymer matrices. Table 6 compares the mechanical, thermal and electrical properties of CNT with the traditional bulk forms.

Because of their great strength (Table 6) and low density, carbon nanotubes (CNT) are especially attractive nanocandidates for incorporation into a matrix. Even more attractive than CNT are graphene fragments [44]. The graphene is typically corrugated due to numerous defects introduced during preparation, which is excellent for locking the material into the polymer (whereas CNT surfaces are usually smooth and defect-free). Per unit weight, the graphene anyway gives double the interfacial area compared with CNT (which are, essentially, rolled up graphene). An additional advantage is that small sheets are much better at intercepting cracks in the composite than small cubes. This kind of composite in effect overcomes the reverse Hall–Petch relationship that prevents grain size being usefully decreased down to the nanoscale in order to strengthen a material [67].

Table 6. Some mechanical properties of bulk and nanoscale carbon materials.[a]

Property	unit	diamond	graphite	CNT
Young's modulus	N m^{-2}	10^9	10^{10}	10^{12}
Thermal conductivity	W m^{-1} K^{-1}	2000	20	3000

[a] The given values are only approximate, in order to enable a rough comparative idea of the material properties to be formed. Actual measured values still depend on many experimental details.

Apart from mechanical strength, another bulk property that might be modified by the admixture of nano-objects is electrical conductivity. For this purpose long metallic carbon nanotubes (for which the percolation threshold is a very low volume fraction, of the order of 1% or less, due to the extreme elongation) are attractive (see the main discussion in Section 8.3).

10.6 Other coatings

Some coatings are merely nanocomposites created in the form of a thin film. For example, ultrahard nanoparticles may be dispersed in a matrix and applied to an object as a surface coating in order to increase wear resistance. Fragments of nanoplates (typically commercially available clays) greatly reduce the gas permeability by increasing the tortuosity of diffusion. In other cases the material of interest is applied directly to the surface of the object, such as the layers of WS_2 discussed in Section 10.3. Combinations are possible; for example, soft transition metal dichalcogenides can be codeposited with a hard ceramic such as TiAlCrN to confer good wear resistance in addition to the low coefficient of friction (level 5–6).

In the case of nano-object-enhanced matrices, typical property improvements (relative to the pure matrix) are a few tens to hundreds of percent.

In other cases, more sophisticated nanostructure is directly responsible for the enhancement of property. A good example is the zirconia-based thermal barrier coatings (capable of delivering a temperature drop now approaching 1 °C per μm) already used on turbine blades in the combustion chambers of jet engines. It is believed that a peculiar nanocolumnar structure that spontaneously develops during physical vapour deposition contributes to achieving the high temperature drop. Furthermore, by incorporating rare earth-enriched nanoclusters within the zirconia, the material acquires a temperature-dependent fluorescence that can be used to monitor the local temperature. The main difficulty in their exploitation to, for example, missile nose cones (to protect them from heating due to high speed passage through the air) is the need for the object to be coated to be placed inside a vacuum chamber. Large vacuum chambers are, however, available and nose cones of the order of 1 m in length could be handled. This technology can be considered to have reached at least level 4.

Physical vapour deposition (e.g., sputtering) is typically used to apply nanoscale coatings. This requires expensive infrastructure and must be carried out under vacuum. Another approach is alternating polyelectrolyte deposition (APED), also known as layer-by-layer (LbL) deposition. It makes use of the fact that many materials become electrified when immersed in water, due to the dissociation of ionized groups such as hydroxyl. For example, titanium naturally coated with an ultrathin film of titanium dioxide will become negatively charged. If it is then immersed in a suspension or solution of positively charged nanoparticles or polyelectrolyte molecules it will become coated and positively charged. After rinsing, the object can then be immersed in a suspension or solution of negatively charged nanoparticles or polyelectrolyte molecules and will become negatively charged [36]. The key feature is that at each step the electrostatic charge is not simply neutralized but reversed. The process can be iterated *ad libitum* in the case of polyelectrolytes to build up a layer of any desired thickness.

10.7 Biomimetic materials

Biology has attracted attention because of its core feature, adaptability. Therefore, biological materials and structures provide inspiration for responsive and smart artificial materials and structures. This is a ubiquitous property of proteins, but most proteins are too fragile to be used in the environment of a missile, and even though the design principles are understood, it is too difficult for present technologies to construct artificial mimics; this is something that really will

have to wait for the development of assembler-based nanomanufacture. Other features of biology include composites—the classic material is wood; again, the design principles are understood (e.g., the key to its remarkable properties is its hierarchical structure right down to the nanoscale, not mimicked in existing artificial composites)—and miniature motors, both linear (e.g., muscle) and rotary (e.g., the common enzyme ATPase). Here too the design principles are understood, but artificial fabrication to this degree of (nanoscale) precision is not yet attainable using available technologies. Hence, the military applications of bionanotechnology in this sense are still at level 0.

10.8 Nanoscale actuators

Another zone of biometic possibilities concerns materials "smart" enough to be classed as devices (actuators). The nano paradigm for such devices is biological muscle. The actual artificial mimics of muscle action work, however, totally differently—they are essentially gels whose volume depends on external factors. This is a well researched area. The main disadvantage is the relatively slow actuation time. Hence, their domain of application is most likely to be as assistants to prostheses. The rapid actuation so characteristic of animal striated muscle is likely to require a somewhat similar architectural design, but such is the sophistication of the proteins involved it is currently difficult to see how they can be replaced by inorganic miniature machines. In the long-term such devices could presumably be fabricated using assembly with atomic precision—at least we now know the principles according to which they are constructed.

A successful recent example of this kind of device is based on the reversibly changeable stiffness of creatures such as the sea cucumber. Their dermis consists of a potentially stiff fibrous filler interacting via chemically controllable hydrogen bonds embedded in a low modulus matrix. Mimicry has been demonstrated by embedding cellulose whiskers in polyvinyl acetate, those tensile modulus can be directly switched by several orders of magnitude [51].

11. Conclusions

In conclusion, we seek to approach the question what research is most worth investing in. First, let us briefly recapitulate the states of technology development from the viewpoint of practical requirements:

A. The technology is already developed in some other commercial sphere and merely needs to be adapted (around level 5).
B. The technology has been demonstrated in the laboratory and work is continuing. Its applications are generic (around level 2).
C. The technology is obvious from theoretical considerations but no one has explored it practically (level 0).
D. Some hints for the technology are extant (e.g., through biomimicry) but no serious effort to develop it has yet been made (level 0).
E. New fundamental insight is required (below level 0).

Nanotechnology in state A raises some particular issues because of the immense variety of possible outputs. This is particularly an issue with composites created from two or more components. The general principles appear to be understood but the parameter space is so vast

that only a very small volume has been experimentally investigated. If a particular requirement (e.g., for a coating with enhanced anti-abrasion properties) is identified and quantitatively specified, it is unlikely that a material with exactly the required properties has already been formulated, but from theoretical knowledge and an examination of existing (i.e., reported) experimental work, informed by constraints of environment, materials and cost, should clearly reveal what development work still needs to be carried out. This also applies to multifunctional materials. It might well be that the desired functionalities have been individually investigated, but not in combination.

Particularly regarding energy sources and storage (i.e., batteries), it may be supposed that any really promising development at state B will be commercialized. This also applies, to a lesser degree, to energetic materials (i.e., propellants and explosives). It should be emphasized that novel items in this category are typically very far from commercialization when reported. There might, indeed, be no practicable route to large-scale manufacture.

The payoffs from research in categories C and D are potentially very large. Of course, if results from the work are published as it proceeds, all will benefit and many may end up participating. Research of this kind might, therefore, be worth developing privately until an advanced stage (at least that of patentability) is reached (cf. float glass, developed by Pilkington). This obviously requires a large and long-term commitment.

11.1 Near-term development, within 5 years

General challenges of this kind of work include ensuring adequate storage stability of high-energy materials and sourcing components (electronic, chemical etc.). There is no really satisfactory approach to accelerated aging, hence definitive assessment of storage stability needs to wait for the results of trials that may last a decade or more. Regarding the supply chain for the components of finished nanomaterials products, the present situation is extremely unsatisfactory because of the lack of a transparent, open market and because of the lack of standards. Both these issues are being addressed [34, 39].

The "low-hanging fruit" comprises nanocomposites in non-structurally critical applications that can replace non-nanomaterials with minimal effort. If the exact material (which may be multifunctional) does not already exist, it may be presumed that extrapolation from existing, published knowledge will deliver a satisfactory recipe that must then be tested and optimized. If there is potentially a very large number of candidate formulations, consideration should be given to automating the formulation and at least some of the testing processes.

11.2 Near-term research, followed by development

Coatings for a variety of functional enhancements, many of which are currently at the research stage elsewhere, for a different application, but which could relatively easily be adapted (e.g., thermal barrier coatings being developed for gas turbine engines), seem to be worth pursuing.

The recent demonstration (see Section 10.5) of the remarkable strength of graphene-based composites (representing a significant improvement upon the previous carbon nanotube-based composites) can be anticipated to lead to rapid development. Unless some hitherto unanticipated drawbacks emerge, these materials could be fairly rapidly exploited in certain structures.

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Glossary

AQI,   attrition quality index
AQW,   armchair quantum wire
APED,   alternating polyelectrolyte deposition
CNT,   carbon nanotubes
COTS,   commercial off-the-shelf
CRL,   commercial readiness level
ER,   electrorheological
IT,   information technology
ITRS,   International Technology Roadmap for Semiconductors
NAL,   nanotechnology availability level
NFC,   near-frictionless carbon
NNI,   National Nanotechnology Initiative (USA)
NSR,   next step requirement
SSL,   single spin logic
TIM,   thermal interface material
TRL,   technology readiness level