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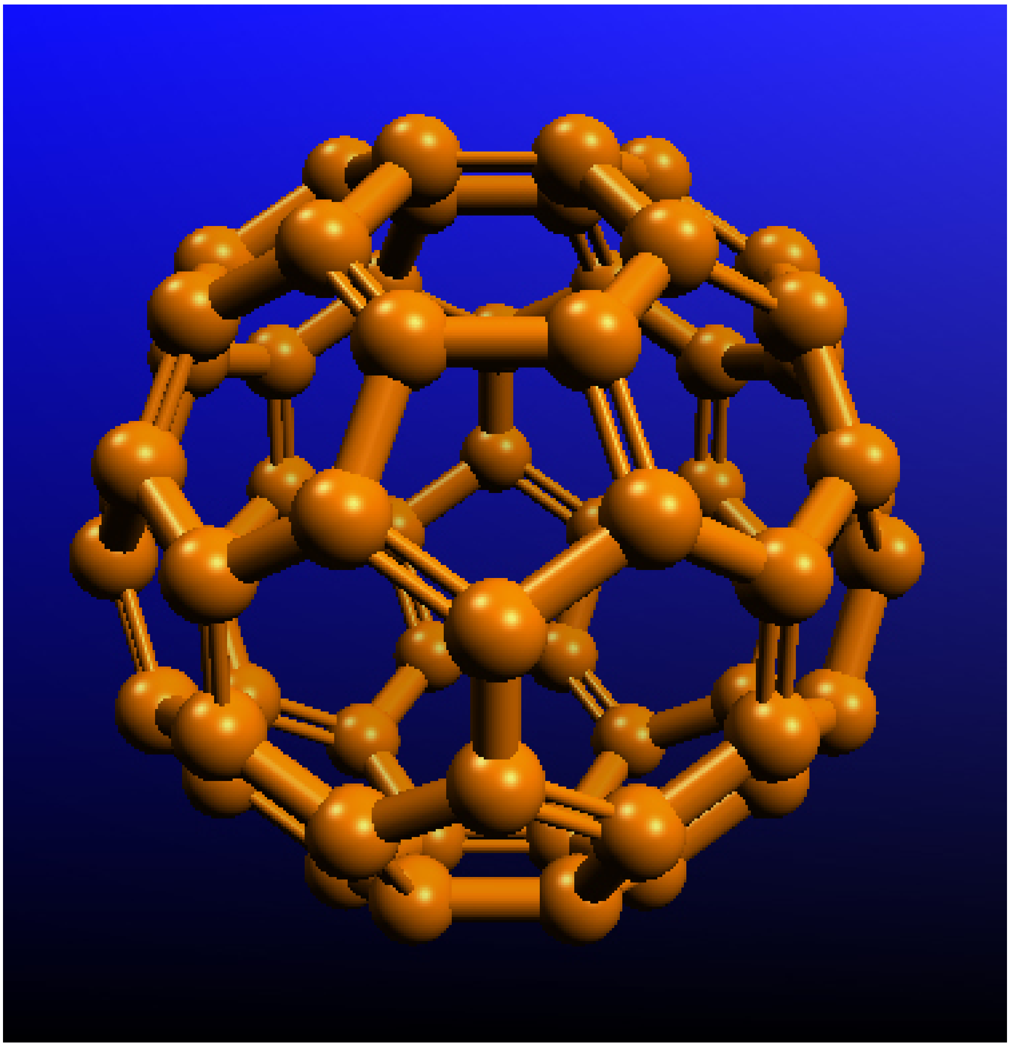
S.J. Savage

Defence applications of new forms of carbon



Schematic model of the C_{60} fullerene molecule (Fagerström, 2003)

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Abstract (not more than 200 words)

This report briefly reviews some applications of new forms of carbon (fullerenes, carbon nanotubes and nanofibres) in military technology. Selected reports are summarised and discussed, and a number of military applications suggested. The report contains recommendations for future studies.

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Rapporten presenterar en kortfattade overblick av militära tillämpningar för de nya typer av kol som har nyligen upptäckts. Ett urval av litteraturen sammanfattas och diskuteras, och ett antal militära tillämpningar föreslås. Rapporten innehåller rekommendationer för fortsatt studier.

Nyckelord
nanoteknik, kol, tillämpningar, fullerener, nanorör

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OBJECTIVE

The aim of this report is to highlight some of the potential applications of new forms of carbon in future military technology. The report is based on surveillance of the scientific literature, participation in conferences and workshops and on personal contacts and experience. It is not intended to be comprehensive, but rather to indicate the range of possible applications as a background to a more detailed investigation and prioritization of military applications.

INTRODUCTION

Carbon, which occurs naturally as graphite and diamond, is one of the most well known elements, and yet in the middle of the 1980's a completely new form of the element was discovered. Kroto, Smalley, Curl and their co-workers were the first to report the existence of the C_{60} molecule, named as buckminsterfullerene and commonly known as "buckyballs" due to the completely spherical shape of the molecule. This was in itself a sensation, which led to the award of the 1996 Nobel Prize in chemistry to Kroto, Smalley and Curl. Buckminsterfullerene was found to be only one of a family of related molecules, frequently simply referred to as fullerenes. However, only a few years later in 1991 Ijima was able to prove the existence of yet another new form of pure carbon, this time in the form of tubes of carbon molecules, known as nanotubes. Since then, and concomitant with the rapid expansion of the field of nanotechnology, much attention has been paid to carbon and related compounds, an interest driven by the unusual and extreme properties of fullerenes, nanotubes, nanofibres and compounds derived from these macromolecules.

Fullerenes, nanotubes and their compounds have been shown to possess a wide range of properties which are especially interesting for practical applications. Properties of especial interest include chemical, electrical, electronic, thermal, and mechanical.

It is interesting to note that observations of hollow carbon fibres with nanometre dimensions were documented by Swedish scientists (Hillert and Lange) as early as 1958 [1].

PRODUCTION METHODS

It is not the purpose of this report to review the wide range of production methods which can be used to produce fullerenes, nanotubes and their compounds. Those methods which are well known are more than adequately described in the literature; see for example the book by Dresselhaus et al [2] or the reviews by Dai [3], and Journet & Bernier [4]. Huczko has reviewed techniques for production of *aligned* nanotubes [5], and Ravary [6] has reviewed production of carbon nanostuctures from a Scandinavian perspective. In general it can be said that the main difference between production methods is that some are designed to produce carbon nanotubes in the free state, i.e. not bound to a surface, and other methods are designed to produce nanotubes, sometimes with a particular orientation, on a substrate. The latter methods are especially interesting for (nano)electronics, using nanotubes as electronic devices in transistors, diodes and similar applications.

Very briefly it can be said that nanotubes and fullerenes are produced by "condensing" carbon under extreme conditions. The original method used was to evaporate carbon thermally, using the high temperatures available in an electric arc or by directing a laser beam on a carbon sample. More recently carbon nanotubes have been produced by decomposition of hydrocarbon gases such as methane using a catalyst such as a nickel-iron alloy. The latter method is preferred for large scale production of carbon nanofibres, and has been reviewed by

Rodriguez [7]. While nanofibres do not have such extreme mechanical properties as nanotubes, the relative simplicity of the production method allows a more economic production, and the properties are more than adequate for many applications. It should be emphasised that production techniques are under intensive development at the present time, and the situation will likely be quite different in the next few years.

COSTS

The cost of producing carbon nanotubes and fullerenes has frequently been cited as the most important factor in limiting the use of these materials in practice. It has been said that with the exception of scientific instruments, the cost of nanotubes will prohibit any practical uses. Initial prices of US $1000/gram for high purity nanotubes seemed to support this statement only a few years ago. However, the extreme properties of nanotubes has stimulated intense interest in development of more economical production methods, and several companies are now claiming production levels of several 10's of thousands of kilograms/year, with prices expected to fall by a factor of 1000 to around US $1/gram within a few years. Today carbon nanotubes can be bought for about US $2/gram [6, 8]. Already there are reports that lower quality carbon nanofibres are being used in the automotive industry to produce electrically conductive paints to improve the electrostatic painting process. There is a list of approximately twenty companies producing and supplying carbon nanostructured materials available on the internet [1]. In the Scandinavian area there are some activities to begin producing carbon nanotubes commercially at n-Tec and SINTEF (Norway) and a company associated with VTT in Finland.

PROPERTIES AND APPLICATIONS

Fullerenes and related molecules

The properties of fullerenes which have attracted most interest by the scientific community are those associated with the symmetrical structure of the fullerene family of molecules, and that the molecule contains only carbon atoms in identical atomic environments. The molecules are completely spherical (in the case of C_{60}, shown schematically on the front cover) or oblate (flattened) or prolate (stretched) spheroids for other members of the family. Being hollow, other atoms can be inserted into the fullerene cage, and studies are currently underway to investigate what effect this may have on properties. A recent book edited by Shinar et al has reviewed the optical and electronic properties of fullerenes and their derivatives [9].

The most immediately useful property (from a military point of view) is the non-linear optical response of the C_{60} molecule. This is strong enough to be of interest in optical limiting devices, and a number of studies of this phenomenon have been reported. See e.g. [10] and references therein. At least one patent has been granted covering the use of fullerenes as optical limiters [11]. Most of the results reported to date have concerned the use of C_{60} in solution (of e.g. toluene) which is not an ideal method. Chen et al [12] have recently succeeded in synthesizing a solid state polyurethane film containing fullerene molecules, which may offer a more practical device. It should be noted that suspensions of carbon black (essentially soot) has been known for many years to be effective as optical limiters [13], but C_{60} appears to have the advantage of a lower threshold.

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[1] http://www.pa.msu.edu/cmp/csc/NTSite/nanotube-sources-com.html, accessed 2003-12-04

Carbon nanotubes and nanofibres

While fullerenes were the first to be discovered, carbon nanotubes and nanofibres have attracted much greater interest from those seeking materials for practical applications.

Carbon nanotubes can be used as individual tubes, for example in nanoelectronic devices, as arrays of oriented nanotubes, for example in low voltage flat screen displays, or as dispersions of nanotubes or nanofibres in a matrix, which may be a polymer (which is most common), a ceramic or a metal. In addition, nanotubes may be dispersed in polymer fibres.

Carbon nanotubes and fibres have diameters of the order of about one nanometre to tens of nanometres. Their lengths may range from a few hundreds of nanometres to (the latest figure) more than 10 centimetres. These lengths in absolute terms are quite short, which poses some problems when developing practical applications. On the other hand, their lengths to diameter ratios are astronomical, ranging from about 100 to over 10 million. In practical terms this suggests their use as mechanical reinforcements in nanocomposites, an application which is being actively explored. However, other properties of carbon nanotubes suggest it will be possible to produce multifunctional nanocomposites, which combine mechanical strength with electrical and thermal conductivity. Mechanically strong capacitors or batteries for electrical energy storage are under investigation for example.

Interest into the military applications of carbon nanotubes has been shown in the USA (Army Science Conference, 2002, [14]), where many contributions were concerned with carbon nanotubes, and in the United Kingdom [15].

Mechanical properties

The mechanical properties of carbon nanotubes are extreme. The tensile modulus of nanotubes range from about 270 GPa to 1 TPa, (the elastic modulus of diamond is 1,2 TPa) with strengths from 11 to 200 GPa [16, 17]. By comparison, the best maraging steel available, with strength of about 4 GPa is relatively weak! As a result of these properties, much interest has been directed towards incorporating nanotubes and nanofibres into matrices, to produce mechanically strong (nano)composites. This is of course a natural extension from the carbon fibre and glass fibre composites we are already familiar with, and which are used extensively in military technology.

Several reviews covering carbon nanotubes composites have been written recently, e.g. [18, 19] and references therein.

One particularly interesting property is the ability to bend nanotubes through acute angles [18], and even to tie knots in them, without breaking!

Nanotubes can today be produced (with difficulty) in lengths of about 10 cm, which is in many cases too short to use in applications where conventional fibres have been used. However, it is possible to produce in the laboratory nanotubes of considerable lengths (10 metres is suggested). While this is still not ideal, it does suggest the use of nanotubes in applications where fibres such as carbon fibre and polymers such as Kevlar are used today.

Carbon nanotubes, due their small diameter can also be used to reinforce polymer fibres, which are then used in conventional applications. One military example is reinforcing poly(p-phenylene-2,6-benzobisoxazole) (PBO) fibre used in body armour, with nanotubes, where it has been shown that a 10% addition of nanotubes to PBO doubles the energy absorption capacity of the fibre, without degrading other properties [20].

Adding carbon nanotubes to polycarbonate, a material commonly used for ballistic protection shows some improvement, although the results are not reported in enough detail to reproduce them [21].

Thermal properties

The thermal properties of nanotubes are excellent. Thermal conductivity parallel to the long axis of a nanotube is considerably greater than that of copper, and twice that of diamond (the previously best known conductor) while normal to the axis conductivity is much lower. This suggests applications in thermal control, e.g. in electronic components, where an array of nanotubes could be used as solid state "heat pipes" to lead heat away from small areas.

While not a nanostructured material, carbon foams have useful thermal properties, as insulating materials. Spradling and Guth have recently reported the thermal insulation properties of low density carbon foams, and demonstrated this in a support for a large mirror intended for space use [22]. As the carbon foam is also electrically conducting it provided electromagnetic shielding and absorption. The foam can resist very high temperatures and heat fluxes without burning, and is low density and stiff. Several defence applications in high velocity missiles come immediately to mind.

Electrical properties

Mention has already been made of the excellent electrical conductivity of nanotubes, parallel to the tube axis. Ando et al [23] have measured this, and shown that current densities of up to 10 million amperes/cm^2 can be passed through nanotubes. This is ten times greater than is possible with e.g. copper conductors. It also appears that electrical conduction in nanotubes occurs ballistically, i.e. the conductivity is independent of the length of the nanotubes[2]. As we may expect much more use of electrical power in future defence technology (in aerospace, surface vessels and ground vehicles) this may allow the use of thinner and lighter cables. This application is being actively pursued by ABB[3]. Naturally, such a property can also be used in microelectronics, for interconnects, where current densities are today reaching such high levels that electromigration and subsequent failure are reaching problematic levels.

Normal to the tube axis the conductivity is much lower, which suggests applications for anisotropic conductors. Depending on the structure of a tube, semiconducting properties can also be obtained, and these have already been demonstrated in transistors, diodes and logic gates [24]. Collins and Avouris have briefly reviewed the (nano)electronic applications for nanotubes [25], and predict that future devices could run at clock speeds of 1 Thz or more, which is about 1000 times faster than today's processors. Nanotube transistors have also been demonstrated in memory devices, with the potential to use much less power than today's equivalents.

The small diameter and high conductivity of nanotubes also suits them for use as electron emitters in low voltage flat panel displays, which are becoming more and more necessary in portable electronic devices such as computers, navigation aids, communications systems. This application has been studied by Gröning et al [26]. Samsung are reported as planning to release a small (5 cm square) display using nanotubes, by the end of the year 2003. The advantage of using nanotubes instead of more traditional emitters such as molybdenum arises from the much smaller diameter of the nanotubes. This can reduce the voltage required from some hundreds of volts to only a few volts.

Carbon nanotubes can be used to store electrical energy in capacitors, or, due to the high storage capacity: supercapacitors and ultracapacitors. These can be used to replace primary (chemical) batteries and secondary (rechargeable) batteries in many devices ranging from portable communications to diesel locomotives in Siberia [27]. Reports that the power density of a carbon nanotubes-based supercapacitor can be twice that of a conventional supercapacitor have been published [28].

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[2] This should not be confused with superconductivity, where the conductivity is infinite.

[3] P. Isberg, personal communication, 11 Nov. 2003

In an interesting concept for multifunctional materials, Dalton et al have succeeded in creating fibres containing nanotubes, which were then woven into a textile, creating a mechanically strong fabric with the ability to store significant levels of electrical energy [29].

Chemical properties

The small diameter and great length of nanotubes lead to a very high surface/volume ratio. This naturally amplifies the properties of any material which relies on interaction at a surface or interface.

One of the most intensively studied properties of nanotubes is their ability to absorb and desorb hydrogen gas. Many studies have been made of nanotubes as hydrogen storage materials (e.g. [30], [31]. It has been demonstrated that hydrogen storage is possible in nanotubes, but at present it seems unclear if the storage capacity is sufficient for this to be commercially interesting. There are reports of hydrogen storage capacities ranging from rather low levels to several tens's of weight percent [32]. The latter are almost certainly erroneous. For hydrogen storage materials to be realistic for automobile transport applications US Department of Transport studies indicate about 6wt% is the lowest acceptable level. Studies of nanotubes do suggest results approaching this level, but there is still considerable uncertainly. The use of hydrogen stored electrochemically in nanotubes as battery electrodes has also been studied. The storage capacity may be high enough to compete with other rechargeable batteries [33]. Using nanotubes in the electrodes of fuel cells can improve their power output by 100% [34].

One specifically military application for hydrogen loaded nanotubes could however be in energetic materials. Hydrogen is an ideal fuel in rocket propellants and explosives, but difficult to incorporate into solid compositions. Carbon black (soot) is often added to explosives to improve electrical conductivity and reduce the risk for static discharge. By combining these functions and using carbon nanotubes to (a) improve electrical conductivity and (b) improve the energy content by using nanotubes "loaded" with hydrogen a multifunctional propellant may be possible. This concept is being investigated by scientists in Canada.

The high surface area/volume ratio suggests using carbon nanotubes as chemical sensors, and this application area has been investigated by many researchers. Chopra et al [35]. In this case gases including ammonia, carbon monoxide, nitrogen and oxygen were detected, at levels as low as 100 ppm. Of immediate application in military technology is the work reported by Noval et al [36] on detection of dimethylmethylphosphonate (DMMP), a nerve gas stimulant. Using a network of carbon nanotubes it was possible to detect DMMP at sub-ppb levels. It is claimed that the sensor network is selective and will not be masked by common hydrocarbon gases and humidity.

Optical properties

As yet, few reports of optical properties relevant to military technology have been published. One relevant paper however was published recently, on non-toxic (infra-red) obscurants [37]. This work was done using blends of conductive polymers, and has been noted, carbon nanotubes can be incorporated into fibres and coatings to control the electrical conductivity. By combining nanotubes with conductive polymer fibres it may be possible to optimise a material for use as a non-toxic infra-red obscurant. As today's materials are based on copper or brass flakes, which are both toxic and difficult to remove from surfaces after e.g. training exercises this would be significant improvement in performance.

Wallerius has recently noted that by creating a composite of fullerene molecules in liquid crystals which is then spun into a film a material very sensitive to light can be synthesized

[38]. It is suggested that this could be used to store large amounts of information as holograms.

Carbon nanotubes composites

Several applications for carbon nanotube composites in polymers are already in commercial production, and undoubtedly many more are under development. Dissipation of static electrical charge on fuel lines is one application. Jamieson [8] writes that “60 % of cars on American roads have fuel lines containing Hyperion’s carbon nanotubes.” The reason for using nanotubes instead of more conventional conductive fillers is that the extreme length/diameter ratios of nanotubes, combined with their excellent electrical conductivity (better than pure copper) allows very low levels of nanotubes additions to be made while obtaining adequate electrical conductivity.

Another application relying on the electrical conductivity of nanotubes in polymers is in plastic automobile components, to make them electrically conductive so as to allow electrostatic spray painting, which is more efficient and less environmentally damaging than conventional spray painting.

A similar defence application which also relies on the electrical conductivity of nanotubes is in aerospace, to coat external surfaces of aeroplanes with an electrically conductive layer to reduce the risk of penetration and damage in the event of lightning strikes. This is becoming more and more important as composites, which have much poorer electrical conductivity than metal alloys are used in greater amounts in aerospace, for wings, fuselage, and rudder and other components. The increasing level of electronics in aerospace also contributes to this problem, due to susceptibility for disturbance or damage by lightning and static charges. Nanotube composite coatings may eventually find use in space applications (satellites) for the same reason.

Control of the electrical conductivity of a surface is also important in signature management, as one method to reduce the radar signature of an object is to utilise electrical losses to dampen reflected signals. The fact that the nanotubes can also contribute to mechanical strength raises the possibility of making strong surface coatings which can carry mechanical loads. By adding only about 1% by weight (0,5% by volume) Qian et al were able to improve the elastic modulus of polystyrene by between 36% and 42%, and the tensile strength by 25% [39]. Today’s radar damping coatings cannot achieve this, and in that sense contribute parasitic weight.

Ceramic nanocomposites have not been studied in as much detail as polymer nanocomposites, but some potential for improved properties has been demonstrated. The principle of reinforcing a ceramic with strong fibres has been known and used successfully industrially for many years, frequently in high temperature furnace applications. As carbon nanotubes are stable up to very high temperatures (about 2800 °C), this may also be an application for ceramics reinforced with nanotubes. Ma et al has shown that silicon carbide reinforced with 10% nanotubes had fracture toughness and strength improved by 10%. This is however far below the improvement expected from calculations[40]. Although these results are disappointing, we can expect improvements from better knowledge of process technology and load transfer mechanisms. Ceramic nanocomposites may find uses in structural radar absorbers, where the possibility to use the electrical properties of nanotubes combined with their mechanical properties will allow multifunctionality.

What appears to be an excellent book covering the subject of nanocomposites has been very recently published [41].

Discussion and Summary

From the above brief review of the properties of fullerenes, carbon nanotubes and nanofibres there can be little doubt that these new forms of carbon have a wide range of exciting properties. In particular when carbon nanotubes are combined with other materials into composites, an even broader range of structural and functional properties can be obtained, many of which have not been available to scientists and engineers previously. To take just one example, a mechanically strong yet flexible textile-like material able to store electric charge opens the way to many new applications both for flexible (literally!) energy storage and for example clothing with functions such as sensing and health monitoring.

Military interest in nanotechnology using these recently discovered forms of carbon is already apparent, from conference presentations, publications in the scientific literature and acknowledgements of financial support.

Much of the interest for practical applications is concentrated to two areas. Firstly, nanoelectronics, where it can be seen that the principle of "smaller, lighter, faster" can be combined with "lower power consumption" is the driving force. While there are certainly military applications for nanoelectronics, the major effort here is coming from civilian organisations and IT companies.

The second area of activity concerns nanocomposites, i.e. polymers, ceramics or metals containing nanotubes or nanofibres. There are many applications for new materials which can without difficulty be incorporated into existing products without major process changes. This has been seen in the automotive industry, which is not renowned for spending more than is absolutely necessary on materials or process development. While some materials are already in use, these are relatively simple, using nanotubes to control the electrical properties of polymers. Similar materials have immediate military uses, in radar absorber to give one example.

Future challenges arise in developing polymer nanocomposites with improved multifunctionality, where combining electrical energy storage in strong and flexible materials has already been developed. Military applications in unmanned autonomous vehicles, particularly miniature such is one obvious area of application.

There are many challenges remaining, but these are in many cases already being addresses. One area, that of material cost, is already showing significant progress, with prices already being reduced by a factor of at least ten. From the military technology point of view the next major challenge is that of developing sufficient knowledge to be able to combine the wide range of possible matrices and additives in ways which will lead to useful materials. Even here, those results which have already been demonstrated are simply a small scratch on the surface of what will eventually be possible. As one evidence of this, NASA has recently commissioned a study of the "space elevator" concept, wherein a long cable would be used to hoist materials and people from the surface of the earth to near earth orbit. The properties of carbon nanotubes are, at least theoretically, sufficient to meet this challenge [42].

The table below summarises a few of the more obvious military applications. Many more can be thought of, particularly in the area of multifinctionality.

Table of applications (in no particular order)

Application	Material	Description
Protection against lightning strike (aerospace)	Polymer nanocomposite coating. Possibility for load carrying function	Polymer containing nanotubes
Protection against static electricity	Polymer nanocomposite coating. Possibility for load carrying function	Polymer containing nanotubes
Radar reflection reduction	Polymer nanocomposite coating. Possibility for load carrying function	Polymer containing nanotubes
Cooling electronics (heat pipes)	Nanotubes or nanotubes composite	Array of parallel nanotubes
Body armour (soft)	Polymer nanocomposite	Organic polymer reinforced with nanotubes
High temperature radar absorbers	Multifunctional ceramic nanocomposites	Ceramics reinforced with nanotubes
Electrical conductors	Nanocomposites	Metals or polymers containing nanotubes
Electrical interconnects	Individual nanotubes in electronic chips	Nanotubes
Very high speed electronics	Individual nanotubes	Nanotubes as electronic devices
Low voltage displays	Nanotubes	Oriented nanotubes on a substrate
Solid rocket propellants	Energetic compositions containing hydrogen loaded nanotubes	Energetic compositions containing hydrogen loaded nanotubes
Nerve agent sensor	Nanotubes	Nanotube arrays
Electrical energy storage: supercapacitors	Nanotubes	Nanotubes in a composite
Electrical energy storage: batteries	Nanotubes	Nanotubes in an electrolyte
Obscurants	Nanocomposite	Nanotubes in fibres
Translucent armour	Nanocomposite	PMMA/polycarbonate containing nanotubes
Optical limiters	Nanocomposite	Polymer films with fullerenes
“Electric” fabrics	Nanotube fibres	Capacitive fibres in a fabric
Fuel cells	Electrodes	Nanotubes in ceramics or polymers
Gas sensors	Nanotubes	Nanotube arrays
Radar absorbing coatings	Nanocomposite	Nanotubes in polymer coatings
Thermal shielding	Carbon foam	Low density, stiff foam

Recommendations

In view of the potential shown new forms carbon, presented briefly above, it is recommended that a more detailed study into the properties which can be obtained from carbon nanotubes/nanofibre polymer composites.
These studies should be focussed on development of multifunctionality, e.g. electrical energy storage/generation combined with properties giving structural stability. This will lead to materials for use in sensor (and correspondingly anti-sensor) technologies.
While there are undoubtedly military applications for nanoelectronics in computing, the technology needed for these applications is being more than adequately addressed by civilian organisations.

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