

Nano works to get it harder

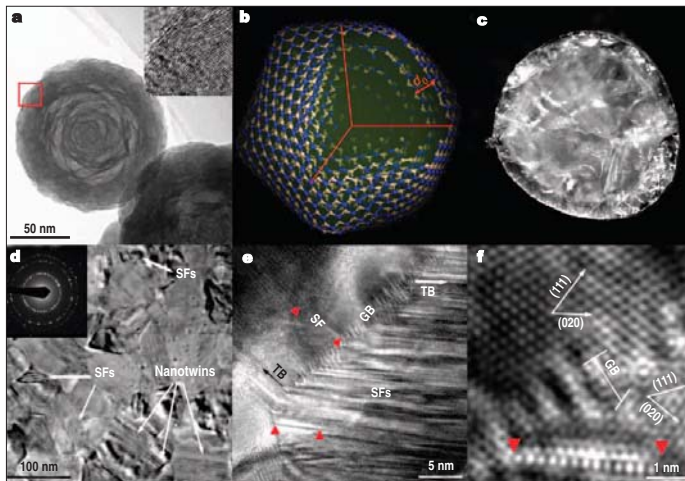
Diamond may yield place to a material that was long on its heels, says s ananthanarayanan

THE diamond-cutting tool has been the last word in hardness for cutting and grinding other materials. Chinese scientists Yungang Tian, Bo Xu, Dongli Yu, Yanming Ma, Yanbin Wang, Yingbing Jiang, Wentao Hu, Chengchun Tang, Yufei Gao, Kun Luo, Zhisheng Zhao, Li-Ming Wang, Bin Wen, Julong He and Zhongquan Liu (two of them in the USA) have found a way to reduce the grain size of *Boron Nitride* to do better than diamond.

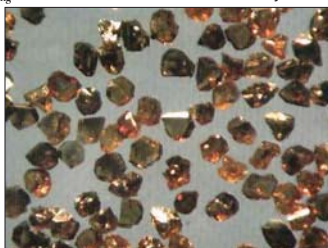
The element carbon, of which diamond is one form, owes its remarkable properties to its atomic structure. Atoms have between one and eight electrons in their outermost electron shell. The cases of two electrons or eight electrons in the outer shell are balanced and stable. Atoms that do not have this structure try, by combining with other atoms, to mutually borrow and lend electrons and get to these numbers. But among all elements, carbon, and some others, have four outer shell electrons that allow these elements to form links with four other atoms, which may be other carbon atoms. This allows a variety of compounds with carbon or other elements and also many geometric forms where an atom shares each of its outer electrons with similar atoms to give both sharing atoms the stability of the "eight electron" state.

Graphite is a form of carbon where carbon atoms form sheets of a honeycomb lattice, which sit on each other. The sheets can slide over each other and graphite is useful as a lubricant. But a different form of carbon, where the atoms take three-dimensional form of interpenetrating cubes, is diamond. This crystalline structure has the feature that it does not present "cleavage planes", where the crystal could disintegrate, and it has tremendous strength, higher than that of other crystal forms. Diamond, thus, shows luster and strength, in contrast to charcoal, which is chemically the same thing, and for its hardness, diamond has extensive industrial use. But as diamond is finally nothing by carbon, it is readily oxidised and cannot be used where there are high temperatures. This is a great limitation of its industrial use.

Another compound that forms this interpenetrating cubic form of crystal is Boron Nitride, or a compound of boron and nitrogen. As boron and nitrogen have three and five outer shell electrons respectively, they form a stable molecule, but when the molecules form crystals they form bonds with four neighbouring molecules, just like the carbon atom. There is, thus, the graphite-like form of layers that slide, which has use as a lubricant and also the cubic form, which is like diamond. This form, known as *cBN*, also has very high hardness. And though hardness is not so high as that of diamond, the *cBN* molecule is not affected by heat and for many industrial uses *cBN* is able to replace diamond.



(a) an image of cBN nanoparticles and (inset) an image corresponding to the position marked with the red box showing defects, including lattice puckering, bending and stacking faults; (b) schematic icosahedral model of a five-shell cBN nanoparticle. d0 is the inter-shell spacing; (c) photograph of an nt-cBN bulk sample with a diameter of about 2 mm; (d) an image of a typical microstructure in nt-cBN. Nanotwins and stacking faults (SFs) are marked (inset, a selected area electron diffraction pattern); (e) an image of nt-cBN showing Shockley partial dislocations (red triangles) emitted from grain boundaries and a high density of stacking faults in twin domains. TB, twin boundary; (f) enlarged image of e, showing the orientation relationship between adjacent nanograins. Boron Nitride cubes (below).



Increasing hardness

Materials are hard because component parts mesh together and resist shearing forces. It has been found that materials formed of smaller crystallites provide more irregularity and less smooth surfaces and thus lead to greater hardness. This kind of hardness is said to arise from grain boundary strengthening or Hall-Petch strengthening, named after EO Hall of the University of Sheffield and PJ Petch of the University of Leeds, who published groundbreaking discoveries during the 1960s. As

it was found that the smaller grain size impeded movement of dislocations and, hence, increased the yield strength, methods have been sought to reduce grain size.

One of the methods has been through heat treatment, which is to control the rate of solidification after plastic deformation by heat. Variations of this method include adding particles during the solidification from the melt, to act as nuclei, or inducing a very small fraction of the melt to solidify at a higher temperature, creating a huge number of minuscule seed crystals. As an equal number of crystallites are formed, the size of grain stays low. Another aspect of grain boundary strengthening is that when the grain size is exceedingly small, this tends to facilitate rather than impede sliding and we have the reverse Hall-Petch effect.

In the case of cBN, very small grain size has been attained by synthetic transformation of other crystal forms, like the graphite-like BN form. This method was first used for creating very hard steel, by rapid cooling or quenching of a form of steel known as *austenite*. Austenite has a face-centered cubic structure and rapid cooling results in the capture of carbon atoms. This, in turn, results in the parent austenite getting

transformed, while cooling, into the body-centered cubic form known as *martensite*, after Adolf Martens, a German metallurgist who developed the technique in the 1860s.

Martensitic transformation of BN has resulted in cBN, with grain size down to 14 nanometres and hardness, which is measured in units of pressure, of 85 billion atmospheres (or *Giga Pascals - GPa*). This hardness is still short of the hardness of over 100 GPa in the case of synthetic diamond, with grain size of 10-30 nanometres.

Chinese transformation

The method the Chinese group has developed brings the grain size of cBN down to 3.8 nanometres and hardness of the order of 100

GPa, which is that of diamond. Going below the level of 14 nm, which is what has been achieved so far, is limited by the high-energy grain boundaries that promote crystal growth.

Attaining "twinning boundaries", or symmetric crystals which attach along matching surfaces, can reduce the boundary energy and make for more stability.

The Chinese group started out with graphite-like sheets of BN and the BN precursor was subjected to *High Pressure and High Temperature* treatment and the crystal structure was monitored using X-Ray interference methods. At 15 GPa and above 1,000°Celsius, the BN material transformed into a translucent cubic phase, mixed with diamond-like structures. At 1,600°Celsius, the material changed completely into *transparent cBN*.

The reverse Hall-Petch effect, which reverses the increase of hardness with reducing grain size, comes into action when the grain size is down to about 10-15 nm, in metals and alloys. cBN with twin domains that was produced by the China team, is seen to continue growing in hardness well below this limit. "Our findings introduce a new strategy and direction in the quest for superhard materials," say the authors in their paper published in the journal, *Nature*.

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Poisoned arrows, snake venom and nerve gases

Understanding various toxins and illustrating how clearly their modes of action can be explained is vital for human health, writes tapan kumar maitra

BECAUSE the coherent functioning of the human body depends so critically on the nervous system, anything that disrupts the transmission of nerve impulses is likely to be very harmful. And because of the importance of acetylcholine as a neurotransmitter, any substance that interferes with its function is almost certain to be lethal. Various toxins are known to disrupt nerve and muscle function by specific effects on cholinergic synapses, so let us consider several of these substances — not only to underscore the serious threat they pose to human health but also to illustrate how clearly their modes of action can be explained once the physiology of synaptic transmission is understood.

Once acetylcholine has been released into the synaptic cleft and depolarisation of the postsynaptic membrane has occurred, excess acetylcholine must



The ribbon structure of the enzyme acetylcholinesterase, which is very essential. Any substances that inhibit its activity are usually very toxic. be rapidly hydrolysed. If this isn't done, the membrane cannot be restored to its polarised state and further transmission will not be possible.

The enzyme acetylcholinesterase is, therefore, essential and substances that inhibit its activity are usually very toxic. One such family of acetylcholinesterase inhibitors consists of *carbamoyl* esters. These compounds inhibit acetylcholinesterase by covalently blocking the active site of the enzyme, effectively preventing the breakdown of *acetylcholine*. An example of such an inhibitor is *physostigmine* (sometimes also called *eserine*), a naturally occurring alkaloid produced by the Calabar bean.

Many synthetic organic phosphates form even more stable covalent complexes with the active site of acetylcholinesterase and are, therefore, still more potent inhibitors. Included in this class of compounds are the widely used insecticides *parathion* and *malathion*, as well as nerve gases such as *sarin* and *soman*. The primary effect of these compounds is muscle paralysis, caused by an inability of the postsynaptic membrane to regain its polarised state.

Nerve transmission at cholinergic synapses can be blocked not only by inhibitors of acetylcholinesterase



A-bungarotoxin (from snakes of the genus *Bungarus*) and cobratoxin (from cobras) are small, basic proteins that bind covalently to the acetylcholine receptor, thereby blocking depolarisation of the postsynaptic membrane. Many natural poisons act as neurotoxins that can cause paralysis leading to death and have functions for defence against predators or in hunting and capturing prey. But some of these natural inhibitors, despite their toxic attributes, are valuable for therapeutic uses at lower doses.

but also by substances that compete with acetylcholine for binding to its receptor on the postsynaptic membrane. A notorious example of such a poison is *curare*, a plant extract once used by native South Americans to poison arrow tips. One of the active factors in curare is *d-tubocurarine*. Snake venoms act in the same way. Both *a-bungarotoxin* (from snakes of the genus *Bungarus*) and *cobratoxin* (from cobras) are small, basic proteins that bind covalently to the acetylcholine receptor, thereby blocking depolarisation of the postsynaptic membrane.

Substances that function in this way are called antagonists of *cholinergic* systems. Other compounds, called agonists, have just the opposite effect. Agonists also bind to the acetylcholine receptor, but in doing so they mimic acetylcholine, causing depolarisation of the postsynaptic membrane. Unlike acetylcholine, however, they cannot be rapidly inactivated, so the membrane does not regain its polarised state.

Though of disparate origins and uses, poisoned arrows, snake venom, nerve gases and surgical muscle relaxants all turn out to have some features in common. Each interferes in some way with the normal functioning of acetylcholine and each is, therefore, a neurotoxin because it disrupts the transmission of nerve impulses, potentially with lethal consequences. Each has also turned out to be useful as an investigative tool, illustrating again the strange but powerful arsenal of exotic tools upon which biologists and biochemists are able to draw upon in their continued probes into the intricacies of cellular function.

The writer is associate professor and head, Department of Botany, Ananda Mohan College, Kolkata

Earth was hit by gamma ray burst

According to scientists, it came from space in the eighth century. steve connor reports

A MASSIVE cosmic explosion in deep space sent out a pulse of high-energy radiation that hit the earth between 774-775 when the emperor Charlemagne ruled much of western Europe, scientists have found. The radiation pulse was probably the most intense cosmic event to have affected earth in the past 3,000 years and it left an indelible imprint in ancient cedar trees dating to that time, they said.



Professor Ralph Neuhauser.



two black holes or two massive stars located between 3,000 and 12,000 light years away, within our own Milky Way galaxy. He said that the cosmic collision caused a "gamma-ray burst" — a flash on intense radiation and one of the most energetic phenomena in the universe. Astronomers have seen them in other galaxies, but never in the Milky Way. "Over the past 3,000 years this was the most energetic event to have hit the earth," Professor Neuhauser said. Even so, it is not likely to have been noticed by anyone at the time because the burst lasted less than two seconds, would not have left a visible impression in the sky and was not close enough to cause species extinctions. "If the gamma ray burst had been much closer to the earth, it would have caused significant harm to the biosphere. But even thousands of

light years away, a similar event today could cause havoc with the sensitive electronics that advanced societies have come to depend on."



Radioactive carbon-14 found in rings of Japanese cedar trees shows that earth had a major influx of cosmic rays about 1,230 years ago.

Professor Neuhauser said. The study is published in the monthly notices of the Royal Astronomical Society.

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