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Glimpses of the Nanoworld

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Abstract

Nano science and technology have added a new dimension to the frontiers of physical and biological sciences. The novel and unexpected properties of novel materials are indeed fascinating and many of them can be exploited for useful applications. In this article, various aspects of nanoparticles and nanotubes are examined. Some highlights of the newly discovered two-dimensional sensation, graphene, are presented.

Historical

The Lycurgus Cup is the only surviving example of a very special type of glass, the dichroic glass. The cup changes colour when it is held up to light. The cup is opaque green but when light is shone through it, it turns to a glowing translucent red cup. This is due to the small amounts of colloidal gold and silver present in it. The cup is an example of 'cage-cup' method of glassmaking. An episode from the myth of Lycurgus is the theme of the scene on the cup. The cup depicts Lycurgus trapped by the branches of a vine and tormented by Dionysus for his cruelty. In the Roman period, colloidal metals were used to dye fabrics, colour glass and to treat diseases. The Romans used metal particles together with glass to achieve dramatic effects. A popular dye, the Purple of Cassius, formed on reacting stannic acid with chloroauric acid is made up of tin oxide and gold nanoparticles. Maya blue used by the Mayas consists of indigo, silica and metal oxide nanocrystals. Damascus swords were first made in the eighth century. They were famous for their strength and sharpness. Peter Paufler and his colleagues in Germany studied samples from the blade of the Damascus sword and found tiny nanowires and nanotubes in the sample. They revealed the first ever carbon nanotubes present in steel. The swords were forged from Wootz steel first made in India around 300 BC.

Nature makes use of nanoparticles for specific purposes. For example, there are bacteria containing magnetite particles which are used for navigation.

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The first laboratory synthesis of nanomaterials was by Michael Faraday in the year 1857, who prepared gold nanoparticles. He called these materials divided metals since he actually did not know their dimensions. What is amazing is that he could make colloidal metal particles dispersed in solvents and recognized that they exhibited different colours depending on the size. Interest in the nanoworld of today seems to have been kindled by the famous statement of Feynman, 'There is plenty of room at the bottom'. Today, the subject has become extremely competitive and sophisticated. We shall now briefly trace the recent developments in this area.

Nanomaterials

More than a decade ago, nano structures fabricated by the manipulation of atoms were demonstrated in the United States in the IBM Corporation as well as in Hewlett Packard laboratories. Today, nanomaterials are made routinely by various methods. Nanomaterials include zero-dimensional nanocrystals or quantum dots, one-dimensional nanowires and nanotubes and two-dimensional nanofilms or sheets. The different forms of nanomaterials of metals, oxides, sulphides and a variety of other materials have been prepared. We can say that given any material, we can make it in the form of some nanostructure.

The main feature of nanomaterials is that their properties depend on size. This is unlike our experience in the normal world. The most well known example is that of cadmium selenide which on optical excitation emits light of different colours depending on the size of the particles. While 3.5 nanometer crystals of CdSe give out green light and 5 nanometer nanocrystals give out red light (Fig. 1). A good example of a size-dependent property in the nano regime is provided by metal nanoparticles. Gold, which is a shining metal, becomes a non-metal when the particle is small. A gold nanoparticle containing about 200 atoms is non-metallic. Small particles of gold (1-2 nm) are chemically reactive and do not exhibit the characteristic absorption band in the visible spectrum due to surface plasmons. Similarly, mercury ceases to be metallic when the particle has less than 250 particles. Small nanoparticles have all the atoms on the surface and the fraction of surface atoms decreases with increase in size.

To prepare nanoparticles, what one does is to choose an appropriate chemical reaction, prepare the particles dispersed in a suitable solvent first, and determine the distribution of size of the particles by electron microscopy. X-ray diffraction gives the structure of the nanoparticles. The structure may or may not correspond to the stable structure. Small particle size often favours metastable structures. Today there are many methods of

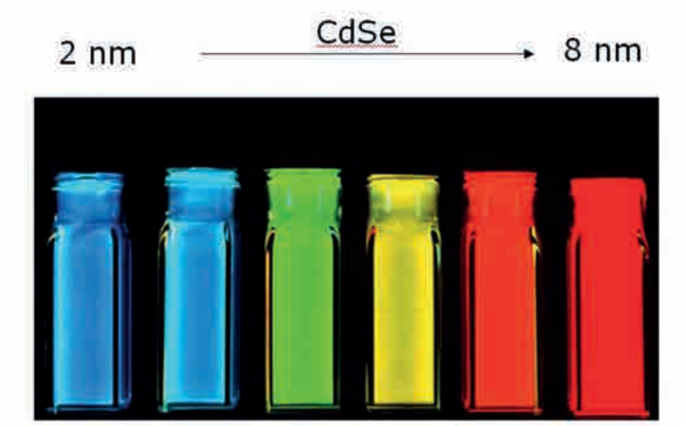

Figure 1. Fluorescence images of CdSe QDs as a function of size.

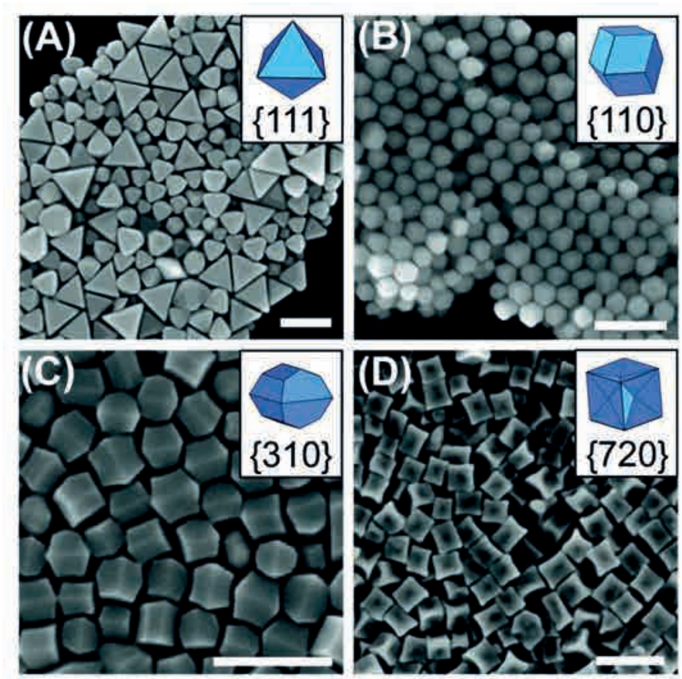

Figure 2. SEM images of (A) octahedra, (B) rhombic dodecahedra, (C) truncated ditetragonal prisms, and (D) concave cubes synthesized from reaction solutions containing Ag^+/Au^{3+} ratios of 1:500, 1:50, 1:12.5, and 1:5, respectively. Scale bars: 200 nm. Note the octahedra form concomitantly with {111}-faceted twinned truncated bitetrahedra, which are larger in size (from Chad Mirkin *et al.*).

making nanoparticles and other nanostructures. Nanoparticles of different shapes have also been generated (Fig. 2). For example, by using the interface between oil and water (or between an organic liquid and water), it is possible to make films of nanocrystals. Carbon nanotubes became famous in the year 1991. They are nothing but extended fullerenes (Fig. 3). They were first made by arc-discharge between graphite electrodes. The deposit near the cathode contains nanotubes. Since then, many methods have been devised to make carbon nanotubes which include the decomposition of metal organic precursors. In the last few years, inorganic analogues of fullerenes as well as nanotubes have been made. For example, nanotubes of molybdenum disulphide, boron nitride and many other layered inorganic materials have been prepared (Fig. 3).

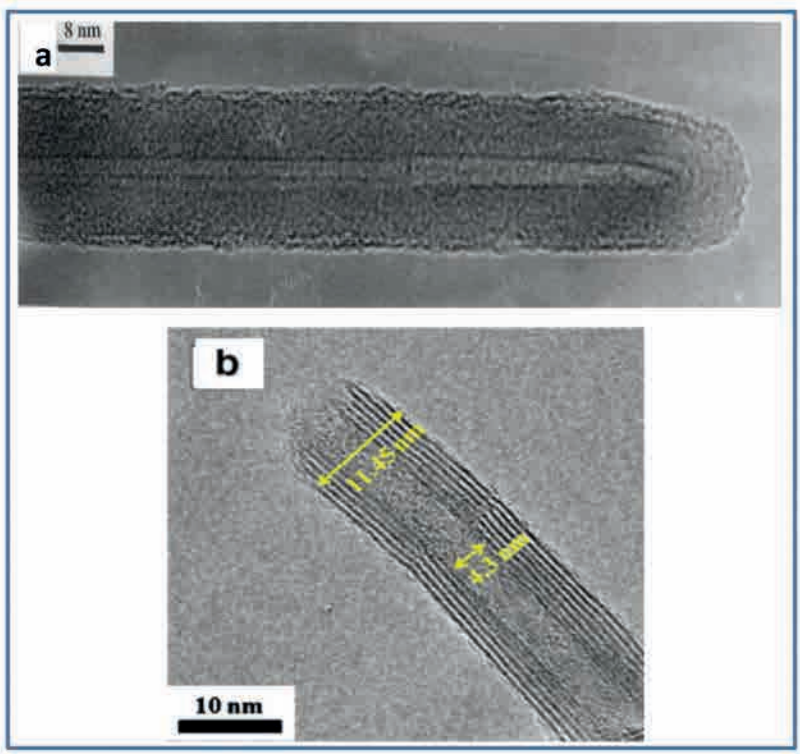

Figure 3. High resolution TEM image (a) of a multiwalled carbon nanotube, (b) of a multilayer TiO_2 nanotube.

Graphene

One of the greatest sensations in physical sciences in recent years is the discovery of graphene with unusual properties. Graphene is nothing but a single two-dimensional sheet of sp^2 bonded carbon atoms. It consists of six-membered rings and shows electronic properties which are most unusual, such as ballistic conduction and high mobility of electrons, quantum Hall effect at ordinary temperatures and a band structure wherein the valence and conduction bands meet at a unique point. A single sheet of such carbon atoms is normally referred to as graphene, but one can have two-, three- and few-layered graphenes as well. Anything beyond ten or twelve layers would be considered to be graphite. Single-layered graphene was prepared a few years ago by using the scotch-tape technique wherein the top layer of a graphite crystal was peeled off. Since then, many chemical and physical methods have been reported for the preparation of single- as well as few-layered graphenes. The edges in graphene sheets which have lone pair orbitals give rise to magnetic properties of these materials. An important form of graphene is provided by graphene nano-ribbons which have even more unique properties. They have more edges. When incorporated in polymers, graphene improves the strength and elastic modulus. Graphene can also be used as a field emitter and an infrared radiation detector. Field-effect transistors based on graphene have been fabricated. Graphene can be doped with elements like boron and nitrogen. Recently analogues of graphene of inorganic layered materials such as molybdenum disulphide and boron nitride have been prepared. They also exhibit certain unusual properties.

Applications

Nanomaterials have found a variety of applications in lithography, photovoltaics, catalysis, nanoelectronics and so on. Thus, many of the nanowires and nanosheets including graphene have been used to prepare field-effect transistors. Dip-pen lithography is a useful technique that makes use of nanoparticles as the ink. Nanoparticles of semiconductors have been used as biological sensors. Nanoparticles of semiconductors and metals can also be used to generate hydrogen. What should be noted is that nanowires of even ordinary materials such as zinc oxide are found to have a variety of applications. Thus, lasers and sensors based on zinc oxide have been fabricated.

Of all the applications of nanomaterials, those in medicine are catching great attention. Thus, gold nanoparticles can be used for destroying cancer cells. The gold particles are directed towards the tumours and on irradiation of these particles, they absorb light and give out the energy as heat. The temperatures reach very high values and burn the cancer cells. Many other types of therapies based on nanomaterials, have been proposed in recent times. Specially noteworthy is the nano nose device prepared in Israel which detects molecules specific to different types of cancers that the patient breathes out. The nano nose is truly impressive. Tissue engineering has emerged to be an important part of nano medicine. Scientists have grown artificial skin, spinal cords and such biologically (and medically) important components of the human body.

Conclusions

Nano science and technology has become the flavour of the day and promises to deliver many new innovations in physical, biological and medical sciences which are of important significance to the welfare of the human beings and society as a whole.