CHEMICAL DESIGN OF MATERIALS

CHINTAMANI N.R. RAO

Introduction

Materials chemistry as we understand it today is of relatively recent origin. A few decades ago, the subject commonly included cement, steel and a few other topics of an applied nature. In the last two decades, the subject has emerged to be recognised as an important new direction in modern chemistry, having incorporated all the salient aspects of solid state chemistry as well. Solid state chemistry is a more formal academic subject representing the chemical counterpart of solid state physics. Materials chemistry, on the other hand, deals with structure, response and function, and has the ultimate purpose of developing novel materials or understanding structure-property relation and phenomena related to materials. Structure and synthesis, which are integral parts of the subject, are fully utilised in the strategies for tailor-making materials with desired and controllable properties, be they electronic, magnetic, optical, dielectric, absorptive or catalytic. The material can be organic, inorganic or biological and can be in any condensed state of matter. Materials chemistry is thus a truly interdisciplinary subject incorporating the principles, systems and practice of all branches of chemistry and is based on sound foundations of physics. What distinguishes the subject from pure solid state chemistry is the ultimate materials objective.

In Table 1, we present a possible description of materials chemistry. With this description, it becomes difficult to classify materials in the way this was done in earlier years when it was common to classify them as ceramics, metals, organics and so on. We now have organic metals, superconductors and non-linear materials, as well as the ceramic counterparts. It is probably more convenient to classify materials using properties or phe-
nomena as the bases for classification. For example, porous solids, superconductors, polymers, ferroics and composites cover all types of chemical constituents. It is, however, common to distinguish molecular solids from extended solids as they represent two limiting descriptions. Another aspect to be noted is that materials chemistry contains all the elements of modern chemistry, such as synthesis, structure, dynamics and properties. In synthesis, one employs all possible methods and conditions from high-temperature and high pressure techniques to mild solution methods (chimie douce or soft chemistry). Chemical methods generally tend to be more delicate, often yielding novel as well as metastable materials. Kinetic control rather than thermodynamic control of reactions favours the formation of such products.

All the available methods of diffraction, microscopy and spectroscopy are used for structure elucidation. For detailed structure determination, single crystals are not absolutely essential. Even powders suffice for the most part because of the advances in diffraction profile analysis. These advances in structural tools enable more meaningful correlations of structure with properties and phenomena. Catalysis is becoming more of a science partly because of our ability to unravel the structures and surfaces of catalysts. We shall examine the nature and scope of materials chemistry by briefly examining the present status of a few typical classes of materials.
What is noteworthy is the ability of chemists to design materials of choice based on their knowledge of structure and reactivity and on their unique skills in the art of synthesis.

Transition Metal Oxides

Transition metal oxides constitute the most fascinating class of materials, and exhibit a variety of structures and properties. The metal-oxygen bond can vary anywhere between highly ionic to covalent or metallic. The unusual properties of transition metal oxides are clearly due to the unique nature of the outer d-electrons. The phenomenal range of electronic and magnetic properties exhibited by transition metal oxides is noteworthy. Thus, the electrical resistivity of oxide materials spans the extraordinary range of $10^{-10}$ to $10^{20}$ ohm cm. We have oxides with metallic properties (e.g. RuO$_2$, ReO$_3$, LaNiO$_3$) at one end of the range and oxides with highly insulating behavior (e.g. BaTiO$_3$) at the other. There are also oxides that traverse both these regimes with change in temperature, pressure, or composition (e.g. V$_2$O$_3$, La$_{1-x}$Sr$_x$VO$_3$). Interesting electronic properties also arise from charge density waves (e.g. $K_{0.3}$MoO$_3$), charge-ordering (e.g. Fe$_3$O$_4$) and defect ordering (e.g. Ca$_2$Mn$_2$O$_5$, Ca$_2$Fe$_2$O$_5$). Oxides with diverse magnetic properties anywhere from ferromagnetism (e.g. CrO$_2$, La$_{0.3}$Sr$_{0.7}$MnO$_3$) to antiferromagnetism (e.g. NiO, LaCrO$_3$) are known. Many oxides possess switchable orientation states as in ferroelectric (e.g. BaTiO$_3$, KNbO$_3$) and ferroelastic [e.g. Gd$_2$(MoO$_4$)$_3$] materials. There is a variety of oxide bronzes showing a gamut of properties. Superconductivity in transition metal oxides has been known for some time, but the highest $T_c$ reached was around 13 K till 1986 and we now have copper oxides with $T_c's$ in the region of 160 K. The discovery of high $T_c$ superconductors focused worldwide attention on the chemistry of metal oxides and at the same time revealed the inadequacy of our understanding of these materials. Recent developments related to colossal magnetoresistance (CMR) have also occurred in oxide materials ($La_{0.7}Ca_{0.3}MnO_3$).

Late in 1986 the scientific community received the big news of the discovery of a high temperature oxide superconductor. The material that was found to be superconducting with a $T_c$ of ca 30 K was based on the cuprate La$_2$CuO$_4$. A yttrium cuprate with superconductivity above liquid nitrogen temperature emerged around March 1987. The compound was known to be YBa$_2$Cu$_3$O$_7$ (Fig. 1). Several families of cuprate superconductors have since been synthesised and characterised and the highest $T_c$ of 135 K is found in
HgCa$_2$Ba$_2$Cu$_3$O$_8$. Under pressure, the $T_c$ increases to 160 K. Most of the cuprate conductors have holes as charge carriers.

Giant magnetoresistance was known to occur in bilayer and granular metallic materials. Perovskite manganates of the general formula Ln$_{1-x}$A$_x$MnO$_3$ (Ln = rare earth, A = alkaline earth) have generated wide interest because they exhibit colossal magnetoresistance (CMR). These oxides become ferromagnetic at an optimal value of $x$ (or Mn$^{4+}$ content) and undergo an insulator-metal (I-M) transition around the ferromagnetic $T_c$. These properties are attributed to double exchange associated with electron hopping from Mn$^{3+}$ to Mn$^{4+}$. The double-exchange which favours itinerant electron behaviour is opposed by the Jahn-Teller distortion due to the presence of Mn$^{3+}$. Application of magnetic fields causes CMR around $T_c$ (Fig. 2). The manganates show charge ordering especially when the average size of the A-site cations is small. Charge ordering also competes with double exchange and favours insulating behaviour. Thus, the manganates exhibit a variety of properties associated with spin, charge as well as orbital ordering.
Fig. 2: Temperature-variation of (a) the magnetization, (b) the resistivity (at 0 and 6T) and (c) the magneto resistance in La$_{0.8}$Ca$_{0.2}$MnO$_3$. 
Synthesis of Materials

Although rational design and synthesis have remained primary objectives of materials chemistry, we are far from achieving this goal fully. There are many instances where rational synthesis has worked (e.g., porous solids), but by and large the success is limited. Thus, one may obtain the right structure and composition, but not the properties. There are very few examples where both the structure and properties of the material obtained are exactly as desired. The synthesis of ZrP$_{2-x}$V$_x$O$_7$ solid solutions showing zero or negative thermal expansion is one such example. The synthesis of HgBa$_2$Ca$_2$Cu$_3$O$_8$ with the highest superconducting $T_c$ (ca. 160 K under pressure) is another example. One may also cite examples of the synthesis of ionic conductors and other materials. Most inorganic materials are still discovered accidentally, the cases of high $T_c$ cuprates and CMR manganates being well known. What is significant is the development of new strategies for synthesis, particularly those involving soft chemical routes. These methods are ideal in obtaining novel metastable materials.

The methods of soft chemistry include sol-gel, electrochemical, hydrothermal, intercalation and ion-exchange processes. Many of these methods are employed routinely for the synthesis of ceramic materials. There have been recent reviews of the electrochemical methods, intercalation reactions and the sol-gel technique. The sol-gel method has been particularly effective with wide-ranging applications in ceramics, catalysts, porous solids and composites and has given rise to fine precursor chemistry. Hydrothermal synthesis has been employed for the synthesis of oxidic materials under mild conditions and most of the porous solids and open-framework materials using organic templates are prepared hydrothermally. The advent of supramolecular chemistry has also made an impact on synthesis.

Many of the traditional methods continue to be exploited to synthesise novel materials. In the area of cuprates, the synthesis of a superconducting ladder cuprate and of carbonato- and halocuprates is noteworthy. High pressure methods have been particularly useful in the synthesis of certain cuprates and other materials. The combustion method has come of age for the synthesis of oxidic and other materials. Microwave synthesis is becoming popular while sonochemistry has begun to be exploited.

There are several reviews specific to the different families, such as layered transition metal oxides, metal phosphonates, and metal nitrides. Precursor synthesis of oxides, chalcogenides and other materials is being
pursued with vigour. Thus, single-molecule precursors of chalcogenide containing compound semiconductors have been developed. Molten polychalcophosphate fluxes have been employed for the synthesis of complex metal thiophosphates and selenophosphates. Precursor carbonates are effective in the synthesis of many oxide materials. Electrochemical techniques have been useful in oxidation reactions (e.g., preparation of SrCoO₃, ferromagnetic LaMnO₃ containing ca. 30% Mn⁴⁺, La₂NiO₄₋₂₅, La₂CuO₄⁺). Intercalation and deintercalation of amines can be used to produce novel phases of oxides such as WO₃ and MoO₃. Topochemical oxidation, reduction and dehydration reactions also give rise to novel oxide phases, which cannot be prepared otherwise. Thus, La₂Ni₂O₅ can only be made by the reduction of LaNiO₃. Special mention must be made of the simple chemical technique of nebulised spray pyrolysis of solutions of organometallic precursors, to obtain epitaxial films of complex oxide materials; this technique can also be used to prepare nanoscale oxide powders. Epitaxial films of PZT, LaMnO₃, LaNiO₃ and other oxide materials have been prepared by this method.

Molecular Materials

Molecular materials, especially organic ones, have gained prominence in the last few years, with practical applications as optical and electronic materials already becoming possible. This area of research has benefited from attempts to carry out rational design based on crystal engineering and supramolecular chemistry. Polymer research has become more focused on developing new synthetic methods and controlling polymerisation. Since architecture and functionality at a molecular level control many of the properties of polymers, there are efforts to synthesise polymers with well defined topologies. Polymers involving rotaxanes, catenanes, rods, dendrimers and hyperbranched systems are some recent examples of such efforts. Recognising that hydrogen bonding is the driving force for the formation of crown ether based polyrotaxanes, mechanically linked polymers have been prepared with the possibility of molecular shuttles at polymeric level. New synthetic routes for dendrimers and hyperbranched polymers suggest many new possibilities.

Semiconducting, metallic and superconducting molecular materials have been investigated by several workers in the last two decades. New types of TTF type molecules, transition metal complexes with elongated π ligands, neutral radicals and Te-containing π donors have been synthesised and an
organic superconductor with an organic anion, $\beta^\prime - \text{(ET)\textsubscript{2}}\text{SF}_\text{6}\text{CH}_\text{2}\text{CF}_\text{2}\text{SO}_\text{3}$, has been discovered. Cation radical salts of BEDT-TTF and similar donors as well as BEDT-TTF salts are still a fertile ground for the production of new materials. Synthesis of linearly extended TTF analogues as well as of new TCNQ and DCNQ acceptors have been reported. The use of organic semiconductors as active layers in thin films holds promise, $\pi$-hexithiophene being an example. Organic polymers with a variety of electrical properties have been characterised over the years.

Molecular magnetic materials constitute an interesting area of research, although practical applications may not be feasible in the short term. Synthesis and design of molecular ferromagnets, ferrimagnets and weak ferromagnets, providing permanent magnetisation with fairly high $T_c$ values are the main objectives of this effort. While purely organic ferromagnets have only reached modest $T_c$s below 2 K, materials incorporating transition metals have shown promise [e.g. V(TCNE)$_3$]. Molecular magnetic materials generally make use of free radicals such as nitroxides, high-spin metal complex magnetic clusters or a combination of radicals and metal complexes. There has been renewed interest in spin-crossover materials with emphasis on active elements for memory devices and light-induced spin changes. The study of diradicals and radical pairs has been strengthened by our understanding of how to stabilise the triplet state. C$_{60}$-TDAE ($T_c = 16$ K) and related compounds have attracted some attention (TDEA = tetrakisdimethylaminoethylene). BEDT-TTF salts with magnetic anions have been discovered. Organometallic materials based on neutral nitroxide radicals and charge-transfer (CT) complexes derived from the radicals have been examined.

High performance photonic devices have been fabricated from conjugated polymers such as poly(p-phenylenevinylene), polyaniline and polycrithiophene. The devices include diodes, light-emitting diodes, photodiodes, field effect transistors, polymer grid triodes, light emitting electrochemical cells, optocouplers and lasers. The performance levels of many of these organic devices have reached those of the inorganic counterparts. The high photoluminescence efficiency and large cross section for stimulated emission of semiconducting polymers persist up to high concentrations (unlike dyes). By combination with InGaN, hybrid lasers can now be fabricated. Plastic electronics is moving rapidly from fundamental research to industrial applications.

The area of molecular nonlinear optics has been strengthened by investigations of three-dimensional multipolar systems, functionalised polymers
as optoelectronic materials, near infrared optical parametric oscillators and related aspects. There have been some advances in chromophore design for second-order nonlinear optical materials; these include one-dimensional CT molecules, octopolar compounds and organometallics. Some of the polydiacetylenes and poly(p-phenylenevinylene)s appear to possess the required properties for use as third-order nonlinear optical materials for photonic switching.

Increasing interest in molecular materials has had an impact on the direction of organic chemistry as well, giving rise to large-scale activity in this area. The discovery of fullerenes and fullerene-based materials has contributed to some interesting developments. Organic-inorganic hybrids offer many interesting possibilities, with the composites exhibiting properties and phenomena not found in either component. Two types of materials can be classified, organic-inorganic units held together by weak bonds and organometallic polymers. Devices have been fabricated making use of self-organised thiols and other molecular systems. Device-related studies of functional polymers have also been fruitful. Devices and assemblies based on Langmuir-Blodgett films are becoming increasingly attractive.

Porous Solids

Porous inorganic materials have many applications in catalytic and separation technologies. Zeolites have truly had a great impact on chemical industry and everyday life. The synthesis of microporous solids with connectivities and pore chemistry different from zeolitic materials has attracted considerable attention. A variety of such open framework structures, in particular Al, Zn, and Ga phosphates as well as many other metal phosphates, prepared hydrothermally in the presence of structure directing organic amines, have been characterised. In Fig. 3, we show the structure of a typical open-framework metal phosphate. There have been many break-throughs in the design and synthesis of these molecular sieves with well defined crystalline architecture and there is a continuing quest for extra-large pore molecular sieves. Several types of new materials including tunnel and layer structures have been reported. The discovery of mesoporous silica (pore diameter 20 -200 Å) by Mobil chemists added a new dimension to the study of porous solids. The synthesis of mesoporous materials also makes use of structure-directing surfactants (cationic, anionic, and neutral) and a variety of mesoporous oxidic materials (e.g. ZrO2, TiO2, AlPO4, aluminoborates), have been prepared and characterised.
An appropriate integration of hydrogen bond interactions at the inorganic-organic interface and the use of sol-gel and emulsion chemistry has enabled the synthesis of a large class of porous materials. Today, we have a better understanding of the structure, topology and phase transitions of mesoporous solids. Block copolymers have been used to prepare mesoporous materials with large pore sizes (>30 nm). There is also some understanding of the lamellar-hexagonal-cubic phase transitions in mesoporous oxides (Fig. 4). Derivatised mesoporous materials have been explored for potential applications in catalysis and in other areas it has been found that transition metal complexes and metal clusters encapsulated in cubic mesoporous phases show high catalytic activity for specific reactions. Macroporous solids with pore diameters in the 200-10,000 Å range have been prepared by using polymer spheres as templates. Macroporous-mesoporous silica has been characterised.

Organic inclusion compounds and clathrates have been known for a long time. While these compounds are still being investigated, there have been efforts to synthesise novel organic or organic-inorganic hybrid structures by supramolecular means. The channels can accommodate benzene, xylenes and other molecules and the process is reversible.
Nanomaterials

The synthesis, characterisation and properties of nanomaterials are active areas of research today. Nanostructured materials assembled by means of supramolecular organization offer many exciting possibilities. These include self-assembled monolayers and multilayers with different functionalities, intercalation in preassembled layered hosts and inorganic three-dimensional networks. Based on such materials, nanodevices and nanoelectronics seem to be on the verge of becoming realities.

The structures, electronic properties and related aspects of semiconductor nanoparticles such as CdS, InAs are of great interest. Size-dependent electronic structures of semiconductor and metal nanocrystals have been examined. The reactivity of metal clusters deposited on solid substrates varies with size. When the cluster size is small (<1 nm), an energy gap opens up. Bimetallic clusters show additive effects due to alloying and cluster size in their electronic properties. Small metal clusters of Cu, Ni and Pd show enhanced chemical reactivity with respect to CO and other molecules. Interestingly, nanoparticles of gold (non-metallic) exhibit catalytic activity.
Metal clusters and colloids, especially those with protective ligands, have been reviewed in relation to nanomaterials. Methods of preparing nanoparticles of various metals as well as nanocrystalline arrays of thiolised nanoparticles of Au, Ag and Pt have been developed. In Fig. 5, a TEM image of thiol-derivatised Au nanoparticles forming a nanocrystalline array is shown. More interestingly, by using dithiols, it has been possible to accomplish layer-by-layer deposition of dithiol-metal nanoparticle films. This is somewhat similar to the layer-by-layer self assembly of polyelectrolyte-inorganic nanoparticle sandwich films. Such superlattices involving vertical organization of arrays of metal quantum dots may have novel properties.

Intense interest has developed in carbon science ever since the discovery of the fullerenes and nanotubes properties of $C_{60}$ and $C_{70}$. Synthesis and characterisation of carbon nanotubes have commanded the interest of many workers. The opening, filling, closing and functionalising of carbon nanotubes have been accomplished. Since metal particles are essential as catalysts to prepare nanotubes by the pyrolysis of hydrocarbons, organometallic precursors have been employed to generate nanotubes. Single-wall nanotubes have been obtained by the pyrolysis of metallocene...
Fig. 6: Aligned carbon nanotube bundles. (a) and (b) are in two perpendicular directions.
or Fe(CO)₅-hydrocarbon mixtures under controlled conditions. It has also been possible to obtain copious quantities of aligned-nanotube bundles by the pyrolysis of ferrocene (Fig. 6) C-N, C-B and B-C-N nanotubes have been prepared by precursor pyrolysis as well. By using acid-treated carbon nanotubes as templates, ceramic oxide nanotubes have been prepared. Y-junction nanotubes have been prepared by precursor pyrolysis. These may be useful in nanoelectronics. The main applications of carbon nanotubes are likely to be in field-emission devices (display), hydrogen storage and as components of composite materials. Nanotubes of metal chalcogenides have been prepared and characterised.

Concluding Remarks

The above presentation should suffice to indicate the nature and potential of the chemical design of materials. Because of limitations of space, many classes of materials have not been covered. Thus, metal fluorides, nitrides and chalcogenides have not been covered here. Similarly, there is considerable development in areas of biomolecular materials as well as inorganic magnetic, non-linear, and luminescent materials. There has been a vast amount of work on ionic conductors which has been of great value in battery development. Amorphous materials, including glasses, constitute yet another area of great interest today. Computer simulation and methods of theoretical chemistry are constantly employed to unravel the structure and properties of materials. Chemists are making use of the lessons from nature in the design of materials. Biomineralisation is one such aspect. In spite of some success in understanding the way nature designs and builds structures such as those in sea shells and diatomaceous silica, one is far from really imitating, reproducing or excelling nature.