Chemistry of Materials

A Letter to a Young Friend

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My dear young friend

I am really glad to have this opportunity to write to you, specially about a subject in which I have worked for half a century. When I was your age, if somebody had told me that I would be working in chemistry of materials most of my life, I would not have believed it. At that time, chemistry of materials meant studying something about cement, steel, sand and asbestos. It was indeed dull. I never did well in school and college exams on questions related to this subject. Much later in my life, I got greatly interested in the subject for various reasons. First, in my study of chemistry, I was influenced by Linus Pauling who is my academic grandfather. His book titled 'Nature of the Chemical Bond' which I read when I was young made a great impression. It taught me how the structure of molecules and materials is an extremely important aspect of chemistry, and how the understanding of structure and bonding provides a basis to understand chemistry and to do new chemistry. It is because of this terrific inspiration that I started studying chemistry. It was clear at the end of my undergraduate career that I wanted to be a chemist.

It was at Purdue University when I was finishing my work for the PhD degree (around 1957), that a friend of mine came to me with a sample of spectroscopically pure TiO_2*. "What is the structure of this?", he asked me. He thought that it had the rutile structure. "Why don't we determine the structure?", I asked. He wanted me to do this for him. I took the X-ray diffraction pattern with the diffractometer in the physics department and found that it had the anatase structure which is the other form of* TiO_2*. We spent some time to investigate when and how pure anatase transforms to the rutile structure. This is one of the early papers on solids that I published. My interest in the subject continued as I started looking at papers of a similar nature and started publishing little notes here and there. Then I thought that I should study the chemistry of solids more, to understand their transformations, properties and other aspects. Thus, my early work as an independent researcher related to such things as structural transformations in oxides, halides, etc., decomposition and oxidation of solids, and properties of solids such as* *electrical conductivity as a function of composition. As time went on, my interest in the subject increased because of the way the subject transformed.*

The story of Chemistry of Materials is quite interesting. It is not as if chemists straight away started working on the subject as we understand it today. It has taken quite some time for the subject to develop to the present stage. In the 1950s, very few chemists were working in an area which was known as Solid State Chemistry. Most of the solids were inorganic. The prime concern at that time was to understand what we meant by stoichiometry. The problem was the following. There are compounds like NaCl which were easy to understand, with one Cl for every Na. But, there are also other compounds which have unusual compositions such as Pr_6O_{11} *and* Ti_4O_7. *If we assign a charge or oxidation state of –2 to oxygen, Pr and Ti will end up with non-integral charges or oxidation states. How does one rationalize compositions of this kind? This was a big puzzle for chemists. There were people who thought that compounds were not necessarily stoichiometric. Then, how does one explain the absence of simple stoichiometry? It was only in the late 1960s that we understood that such unusual compositions arose because of new types of structural manifestations in solids. They were not due to the presence of defects like vacancies. The subject of solid state chemistry gained maturity by the 1960s. You will be surprised to know that there were no journals to publish research papers in solid state chemistry at that time. It was only in 1968 that the first journal devoted to solid state chemistry was established. (Today, we have several journals dealing with chemistry of materials). As time went on, people worked on many aspects of solid materials particularly metal oxides of various kinds. Then started intense activity in other classes of materials, including organics.*

It is no surprise that in the last few years, the two main streams of chemistry are directed towards biology and advanced materials. It is also not difficult to understand why chemists are getting more and more interested in materials. After all, the quality of life of human beings is directly related to the availability of materials of various kinds. When I say materials, these are not just common materials such as wood, coal, cement and steel, but the vast variety of materials required for electronics, computers, transportation, energy, etc. Materials chemistry encompasses all kinds of materials, organic, inorganic and biological. Materials chemistry deals with materials of all kinds and in all states of matter (Figure 1). They can be glassy, they can be crystalline, they can be liquids, they can be soft solids and they can be hard. The materials may have one of many properties, be they electronic, magnetic, dielectric, mechanical, adsorptive or catalytic.

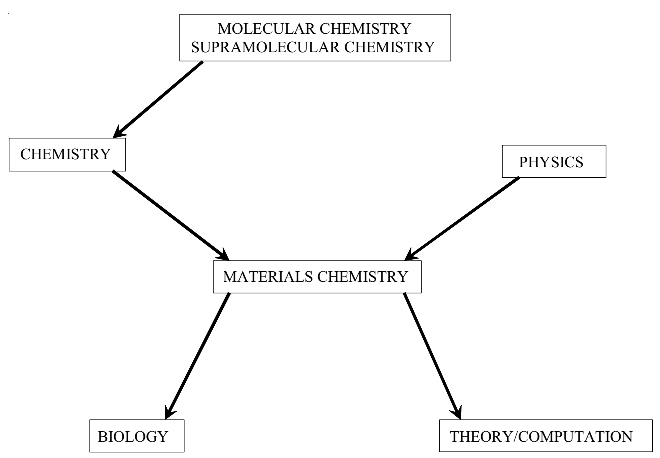

Figure 1. What constitutes materials chemistry.

Tailor-making materials with desired or controllable properties is one of the prime objectives of materials chemistry today.

I mentioned that metal oxides have constituted a major area of work in the chemistry of materials. You may ask why metal oxides? Metal oxides form a class with the widest range of properties. There are oxides which conduct like metals, and there are oxides which are superconductors. There are also oxides which are the best insulators or dielectrics. Some oxides are magnetic. Metal oxides, therefore, have occupied the attention of solid state chemists in a big way. Chemists have synthesized oxides of various structures and properties. I remember in the 1960s, an oxide of rhenium, ReO_3, was made. ReO_3 looks like copper and conducts electricity like copper. It made big news. Soon, many other materials of this kind were discovered. There are also metal oxides which are metallic like copper at certain temperatures and become insulators like wood at lower temperatures. Such properties aroused much interest in me and others.

The culmination of the interest of chemists in metal oxides was when high-temperature superconductivity was discovered. This was in late 1986. Till then, the highest superconducting transition temperature known to us was 23 Kelvin. In December 1986, it was announced that there was an oxide containing copper which became superconducting around 35 Kelvin. It broke the 23 Kelvin barrier and created a big sensation. People all over the world started working on superconductors. Chemists contributed in a big way by making a variety of oxides with superconducting properties. The first attempt in 1987 was to make an oxide which became superconducting at or above liquid nitrogen temperatures (i.e., above 77K). Soon, $YBa_2Cu_3O_7$ with a transition temperature of around 90K was discovered. I am glad to have been part of that effort. I have not seen in my life any discovery that has caused greater sensation than high-temperature superconductivity. Thousands

Inorganic	*Organic*
Semiconductors	*Semiconductors*
Metals	*Metals*
Superconductors	*Superconductors*
Magnets	*Magnets*
Ferroelectrics	*Ferroelectrics*
Non-linear optical materials	*Non-linear optical materials*

Table 1. Materials can be inorganic or organic.

of papers have been published on the subject and it has consumed nearly two hundred thousand pages of journal space. The highest transition temperature that we have attained for superconductivity to date is around 135 Kelvin. It is an oxide containing copper, mercury, and barium. If one applies high pressure on it, it becomes superconducting around 165 Kelvin. I am told that somewhere in the world, room temperature is around 160 or 170 K. If so, this material will be a room-temperature superconductor at that place. Ordinarily, in places like where you and I live, we still do not have a room-temperature superconductor. It will be wonderful if somebody can discover superconductivity at room temperature. It would change the world. (Can you guess why?).

Although I have mentioned only metal oxides till now, there are many other classes of inorganic solids such as nitrides and sulphides which exhibit fascinating properties and have immense applications. For example, GaN on excitation gives blue light. If one mixes yellow light with it using a phosphor, we get white light. This is the methodology used for solid-state lighting. In the last two to three decades, organic materials have gained great importance. People have generated organic compounds which conduct like metals. Some also exhibit superconductivity. There are organic magnets. Thus, there are organic materials which exhibit properties similar to inorganic materials (Table 1). Studies of solid state reactions involving organics and the development of the principles of crystal engineering have given rise to a new facet of materials chemistry. It will be of great interest if one can work on materials which have both organic and inorganic parts, what you might call hybrid materials. Properties and phenomena associated with hybrid materials would be most exciting. In the meantime, let me mention something about polymers.

Polymers of various kinds are known. There are structural polymers with high mechanical strength. They are being used everywhere and they can replace steel and other construction materials. Polymers which have unusual electronic and optical properties have been made. There are polymers which give out blue light on excitation, somewhat like gallium nitride. Polymers have been used to make transistors. Novel polymeric devices such as solar photovoltaic cells and transistors have also been made. Polymer electronics or plastic electronics has, in fact, become an important area in the chemistry of materials.

Materials chemistry today makes use of all the advances of chemistry, and tools of chemistry. It applies all available synthetic, structural and theoretical tools. It makes use of novel strategies such as supramolecular organization and self assembly. It uses biological principles and processes. Let me tell you something that may interest you. As you know, Nature makes hundreds of tons of silica every year. It would be nice to know how Nature makes so much silica under neutral pH. People have found that Nature uses a specific protein to hydrolyze silicon compounds to produce silica. Similarly, people have been interested to know how sea shells are made. Sea shells are composed of calcium carbonate. Nature finds the right kind of proteins to build the beautiful shell structures by arranging bricks of calcium carbonate. Some of these shells make use of calcium carbonate, not in the normal calcite structure, but in the metastable aragonite structure.

As you can guess by now, the subject of materials chemistry is becoming more and more interdisciplinary. To really contribute to it, one has to know a fair amount of chemistry and physics, and where necessary some biology. Those who do theoretical and computational work will also require some expertise in mathematics and with computers. This is what makes the subject attractive to me. Important contributions in materials have actually come from such an interdisciplinary approach. I mentioned about superconductivity earlier. It was considered to be a topic in physics, but today after the discovery of higher-temperature superconductivity, it has become part of chemistry as well. In fact, chemistry got its due recognition in the area of materials after the advent of high-temperature superconductivity. In the last few years, many unusual compounds of iron and cobalt have been made by chemists which are found to show superconducting properties.

An important point to remember is that science progresses continuously. This is very much true of materials chemistry. Periodically, there are new discoveries of materials or methods that revolutionize the subject, and change the very direction of

1985	—	*Fullerenes*
1986	—	*High-temperature superconductivity*
1991	—	*Carbon nanotubes*
1992	—	*Mesoporous solids*
1993	—	*Colossal magnetoresistance in rare earth manganites*
2005	—	*Graphene*

Table 2. Some recent discoveries.

the subject (Table 2). Let me give a couple of examples. If you remember, in the year 1985, fullerenes C_{60} *and* C_{70} *were discovered. They were actually made in the laboratory in the year 1990. Soon after it became possible to make fullerenes in the laboratory, a large number of chemists made use of fullerenes in materials design. Fullerenes are being used in a variety of situations. An extended form of fullerene is the carbon nanotube. Carbon nanotubes were discovered in the year 1990 and they have become important materials because of their high mechanical strength and other important properties.*

There is another phenomenon that I would like to mention. This phenomenon is colossal magnetoresistance. Let me explain what magnetoresistance is. If you measure the electrical resistance of a material at some temperature, you get some value. Then you apply a magnetic field. The magnetic field may decrease or increase the resistance of the material. This increase or decrease in resistance due to a magnetic field is called magnetoresistance. If a material exhibits large magnetoresistance at ordinary temperatures, on applying a small magnetic field, it will have tremendous applications in computers and other areas. One of the major discoveries in 1993 was the observation of very high or colossal magnetoresistance in certain oxides of manganese. This subject has given rise to considerable amount of research. You can again see how oxides are important.

Another class of oxide materials called multiferroics is causing great interest in academia as well as in industry. What are multiferroics, you may ask. As you know, some materials are magnetic while some others may show a maximum in dielectric constant at some temperature. Ferromagnetic materials show hysteresis when magnetization is plotted against magnetic field. Some of the dielectrics (ferroelectrics) exhibit spontaneous polarization on application of an electric field and the *polarization shows hysteresis with respect to the electric field. A material possessing such magnetic and dielectric properties simultaneously is called a multiferroic. What would be interesting is if one can find a material which shows electric polarization on the application of a magnetic field, or show magnetism on the application of an electric field. Such a material would be even more interesting. There is considerable activity all over the world to discover new materials which exhibit such properties.*

Porous solids are of great use for adsorbing gases and vapors as well as in catalysis. Don't forget that zeolites are used commonly in various catalytic applications. Zeolites have channels where only molecules of a particular size (and shape) can get in. Solids with micro-, nano- and meso-pores have been made in the last two decades or so. In recent years, compounds with structures similar to zeolites have been made based on metal phosphates, carboxylates and sulfates. Metal carboxylates are specially interesting since they contain both organic and inorganic components. They are hybrid materials. There is much to be done on hybrid materials wherein we use the functionality and flexibility provided by the organic part along with the rigidity of the inorganic units (see Figure 2 for example). One of the useful properties of some of these compounds is their ability to adsorb hydrogen.

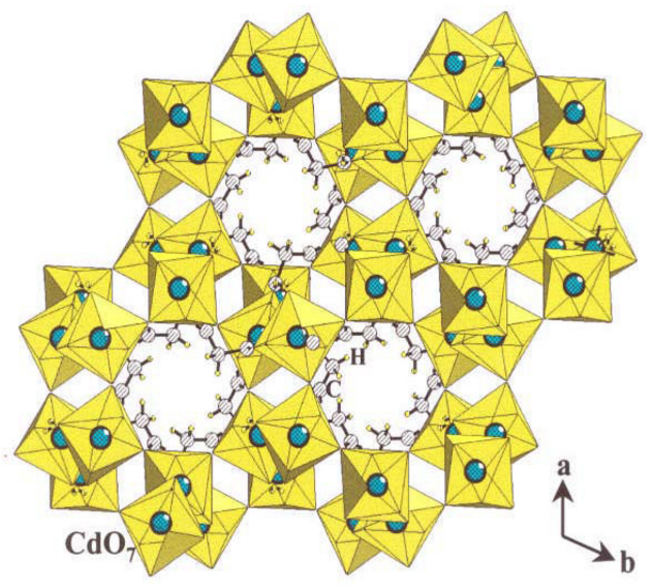

Figure 2. A simple three-dimensional hybrid metal carboxylate.

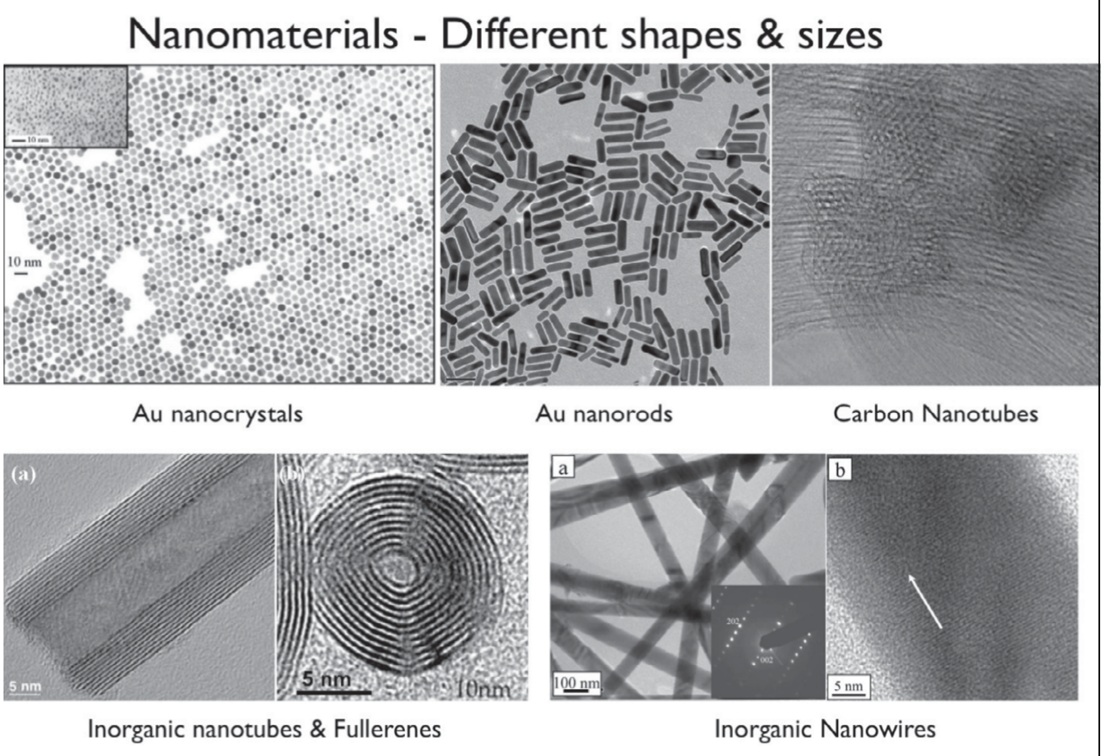

Figure 3. Nanomaterials

In the last few years, nanoscience has become a favourite subject. (Remember a nanometer is 10^{-9} meter or 10 Angstroms). In nanoscience, a high percentage of the work relates to chemistry. Chemistry of nanomaterials which includes synthesis, self-assembly and other aspects is an important aspect of nanoscience. In the last few years, people have made nanomaterials with different dimensionalities – nanorods, nanowires, nano-tubes, nanodots and nanopar-ticles of a large number of inorganic materials (Figure 3). Chemical methods have become essential to make most of the nanomaterials and it appears that we can make almost any material in nanoform by employing an appropriate method. An unique feature of nanomaterials is that size determines their properties. In the nanoregime, new properties manifest themselves due to quantum effects. Nanomaterials have been characterized in various ways, specially by using a variety of microscopes. Many applications of nanomaterials have become possible already. Nanoelectronics still poses many probelms. One challenge would be to incorporate nanoscience with molecular electronics for possible applications.

There are many more materials of equal interest both from the inorganic and organic chemical world. There are several fascinating biological materials. Chemists have tried to mimic biology or find substitutes for natural materials such as bone and the spinal cord. There are several other aspects in biology that have directly influenced the practice of materials chemistry. In addition to solid materials, there is much activity in areas dealing with gels, liquid crystals and such soft materials. Chemistry of amorphous or glassy materials is a vast subject by itself.

I trust that I have been able to give you a flavor of materials chemistry. To be good at it and do something useful, is not only exciting but also demands various types of abilities as I had mentioned earlier. What is really nice is the following. If creativity and innovation are important aspects of science, and necessary needs of society, then materials chemistry has a special place since it requires extraordinary creativity and innovation. One is always creating new materials that didn't exist before. One is finding new properties not looked at before. This fascinates me. Whatever I have tried to do involves creating new materials and looking at novel phenomena. I hope that the subject interests you and other young people. A capable young scientist working in this area can contribute to many aspects which directly deal with the quality of life. Coming to the quality of life, let me say one or two words. Look at the present-day problems of mankind. The pressing problems today have to do with energy, climate and so on. In some countries, safe drinking water is not available. The only way we can solve the problem of energy is by finding the right kinds of materials for beneficiating solar energy and storing hydrogen as well as by designing better batteries and fuel cells. Let us remember that a compound that can store hydrogen upto 6 wt% can be used in a hydrogen fuel cell to run automobiles. All this can happen only with the contribution of materials chemists. Even producing safe drinking water has a component of materials chemistry. One may like to use certain nanomaterials and new kinds of filters for the purpose. I believe, therefore, that there is unlimited scope and unlimited opportunities to contribute to science and serve mankind through materials chemistry.

I can go on and on, but I must stop. You must realize that there are so many classes of materials and so many varied aspects related to them. I cannot possibly mention it all in a little letter, but I hope that this letter has been sufficient to tell you why people do chemistry of materials and how interesting it can be because of its *interdisciplinary and futuristic nature. I do hope to see you one of these days. If you ever decide to work in chemistry of materials, do write to me. You are most welcome to spend some time in my laboratory.*

With affectionate good wishes,

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and
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P.S : *I forgot one thing. Theory and computation have succeeded immensely in the last decade or so in predicting the structure and properties of molecules and materials. So, if one does not like to make or measure, one can calculate or simulate.*

If you and your friends want to read a book that may give an introduction to materials chemistry, I suggest, 'New Directions in Solid State Chemistry' by C N R Rao and J Gopalakrishnan, Cambridge University Press (available as a paper back)

"The devil may write chemical text books because every few years, the whole thing changes."

– *Berzelius (*1779–1849)