Chimie douce: from shake-and-bake processing to wet chemistry

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Opinion

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Wet chemistry methods known as "*chimie douce*" bring together organic and inorganic chemists. They offer new opportunities for the chemist's imagination and lead to the synthesis of novel hybrid or bio-inspired materials.

The development of human civilization, from the Stone Age to modern times, has been related to the nature of the materials man was able to process. Since the very beginning, the development of materials has been based on high-temperature processing. Therefore, fire is undoubtedly one of the most important discoveries of mankind. New materials became available as man was able to produce higher and higher temperatures.

Materials science started at the beginning of the 20th century with X-ray diffraction and quantum mechanics. The fast development of solid state chemistry during the second half of this century was based on the detailed analysis of the structure–property relationships. New materials were synthesized by solid state chemists bringing new ideas from the field of physics. The discovery of high-T_c superconductors is a well-known example of such an interaction between physics and chemistry. Actually, most of these studies were performed on single crystals and solid state chemistry was based on the reaction of powders at high temperature. For the reaction to proceed at a reasonable rate, a high mobility of the reactants and maximum contact surface between the reacting particles are desirable. The rates of these processes are enhanced by higher temperature and finer particle size. As a result, the solid state synthesis of inorganic materials was described as "shake-and-bake".

Living organisms have developed strategies completely different from those used by our materials engineers.[1] Silicate glasses, for example, are made by melting silica sand above 1000 °C, whereas diatoms and radiolarians build sophisticated silica structures at room temperature directly from the very small amount of silica dissolved in seawater. This is a nice example of the "*chimie douce*" (soft chemistry) developed by life to make bio-materials. It is not unique and many other bio-processed materials could be described. They exhibit unique features that can hardly be achieved with our human technology. New chemical routes have to be explored by solid state chemists if they want to compete with micro-organisms.

New synthetic methods, based on wet chemistry, have been developed during the past two decades. They are known as *chimie douce*, a term introduced by French scientists in the seventies.[2] Two routes have been developed, depending on the nature of the precursors.

The first route, starting from solid precursors, was mainly developed by Jean Rouxel, who organized the first international meeting on *chimie douce* in Nantes.[3] It is based on the intercalation properties of low-dimensional solids. Such solids swell in the presence of a solution, allowing faster chemical reactions between ions in the solid layers and solute chemical species in the interlamellar space. These reactions may involve electron (redox) or proton (acid–base) exchange. They are usually topotactic, meaning that the final product retains the memory of the precursor structure. New materials such as TiO_2(B) or VS_2, which cannot be obtained *via* the usual solid state chemistry, have been synthesized.

In the second route, molecular precursors are mixed in solution and transformed into a solid network *via* inorganic polymerization reactions. This is the so-called "sol–gel process" in which metal alkoxides are transformed into oxides *via* hydrolysis and condensation.[4] Several advantages can be put forth to explain the success of sol–gel chemistry. It saves energy, allowing the synthesis of oxide materials at temperatures much lower than with solid state precursors. It is a convenient method for the powderless processing of glasses and ceramics directly from solution. Many industrial applications have been developed during the past few years based on the deposition of functional films *via* techniques such as dip- or spin-coating.

However, *chimie douce* is actually much more than a new process. It develops new chemical concepts and leads to the synthesis of novel materials. The mild conditions associated with the sol–gel synthesis of refractory oxides are close to those used by organic chemists. Hybrid materials in which organic and inorganic species are mixed at the molecular level can then be synthesized.[5] These nanocomposites fill the gap between glasses and polymers and some of them have already been commercialized. Even enzymes and living cells can be entrapped within sol–gel silica. They have been shown to retain their bio-activity after encapsulation and can be used for the realization of biosensors and bioreactors.[6,7] The synthesis of materials by *chimie douce* becomes a meeting point for a wide variety of chemists. They follow different methods and, for molecular chemists, *chimie douce* might be called *chimie dure* (hard chemistry). They have to burn molecular precursors to get ceramics![8]

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