Sonochemistry and its application to nanochemistry

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This article introduces the field of sonochemistry to scientists and to people interested in science. The article presents the principles of the effect of ultrasound radiation on liquids and solutions. In particular, it discusses the applications of sonochemistry to the chemistry of materials. The article emphasizes the activity of my group in the field.

We are all aware of the use of ultrasound radiation in medicine, where it is being used mostly for diagnosis, and where more recently, focused ultrasound radiation is being used to destroy cancer cells. Less is known of its application in chemistry, despite the fact that it has applications across almost the entire breadth of that field. One of the main advantages in conducting sonochemical experiments is that it is very inexpensive to get started in the field. For people willing to learn more about sonochemistry, I suggest refs 1–4.

Let us first address the question of how 20 kHz radiation can rupture chemical bonds, and try to explain the role of a few parameters in determining the yield of a sonochemical reaction and the unique products obtained when ultrasound radiation is used in materials science. To a spectroscopist using $10^{13} - 10^{14}$ Hz radiation to break chemical bonds, this is a puzzle. How is it that 20 kHz ultrasound radiation can do the same job?

A number of theories were developed in order to explain how a 20 kHz sonic radiation could break chemical bonds. They all agree that the main event in sonochemistry is the creation, growth and collapse of a bubble that is formed in the liquid. The first puzzle is how such a bubble can be formed, considering the fact that the forces required to separate water molecules into a distance of two van-der Waals radii would require a power of $10^5$ W/cm$^2$. On the other hand, it is well known that in a sonication bath, a power of 0.3 W/cm$^2$, water is already converted into hydrogen peroxide. Different explanations have been offered; they are all based on the existence of unseen particles, or gas bubbles, that decrease the intermolecular forces, enabling the creation of the bubble. These theories are supported by the experimental evidence, that when the solution undergoes ultrafiltration, before the application of the ultrasonic power, there is no sonochemistry. The second stage is the growth of the bubble, which occurs through the diffusion of solute vapour to the volume of the bubble. The third stage is the collapse of the bubble, that takes place when the bubble size reaches its maximum value. According to the hot-spot mechanism, this implosive collapse raises the local temperature to 5000 K and the pressures to a few hundred atmospheres. These extreme conditions cause the rupture of chemical bonds.

From the time we entered the field in 1993, we were intrigued by the fact that the products of many sonochemical reactions were in the form of amorphous nanoparticles. For example, K. Suslick, who was one of the initiators of the field, has demonstrated that the sonication of Fe(CO)$_3$ as a neat liquid, or its solution in decalin, yielded 5–20 nanometer-sized amorphous iron particles. The reason for the amorphicity of the products is related to the high cooling rates ($>10^{11}$ K/s) obtained during the collapse of the bubble, which does not allow the products to organize and crystallize. These high cooling rates result from the fast collapse that takes place in less than a nanosecond. For this reason, a sonicated solution containing a volatile solute will always lead to amorphous products. However, the reason for the nanometer-sized particles is not yet clear.

The estimated size of the collapsing bubble varies from ten to a few hundred microns. In addition to the region inside the bubble, where a gas phase reaction takes place upon its collapse, a second important region is of great significance. This is the interfacial region, which surrounds the collapsing bubble. Its width is calculated to be 200 nm, and the temperature reached after collapse is 1900 K. Sonochemical reactions of nonvolatile compounds such as salts will occur in this region. In this case, the sonochemical reactions occur in the liquid phase. The products are either amorphous or crystalline nanoparticles, depending on the temperature in the ring region in which the reaction takes place.

We cannot mention here all the parameters (frequency, power, gas under which the sonication takes place, pressure of the gas, etc.) that affect the sonochemical yield and rate, and so we will address ourselves to that one important parameter, of temperature. The equation of an adiabatic implosion is

$$T_{\text{max}} = T_0 \left\{ P_{\text{ext}} (\gamma - 1) / P_{\text{hub}} \right\},$$

where $T_{\text{max}}$ is the temperature reached after the collapse of the bubble, $T_0$ is the temperature of the sonication bath, $\gamma = C_p / C_v$, $P_{\text{ext}}$ is the external pressure equal to the...
sum of the hydrostatic and acoustic pressure, and $P_{\text{sub}}$ is the pressure of the gas inside the cavity, at the radius at which it collapses. The choice of a nonvolatile solvent (decalin, hexadecane, isodurene, etc.) guarantees that only the vapours of the solute can be found inside the cavitating bubble. Thus $P_{\text{sub}}$ is practically the vapour pressure of the solute, and since it is found in the denominator, lower $P_{\text{sub}}$ results in higher temperatures and faster reaction rates.

The conclusion is that the temperature affects the sonochemical reaction rate in two ways. On the one hand, lower temperatures cause a higher viscosity, which makes the formation of the bubble more difficult, and, on the other hand, the dominant effect is that at lower temperatures, higher rates will be achieved in sonochemical processes. This is why the sonic reaction involving volatile precursors is run at lower temperatures. Apparent negative activation energies are measured for sonochemical reactions.

Since 1996, when our first papers began to appear, we have published more than 120 papers describing the preparation of a large variety of nanomaterials, including metals, alloys, metal oxides, metal sulfides, metal nitrides, chalcogenides, metal-polymer composites, ceramic materials, dielectric materials, and others. In addition to the synthetic work, we have developed a number of fields that have emerged from our ability to prepare such a large variety of materials. Below we detail some of these research areas.

The self-assembly monolayer coating of many functional groups, especially thiols on surfaces and particles, have attracted many groups around the world. In about 60% of the reports, gold served as the substrate. 30% of the studies were conducted on silver and 10% on copper. We have coated Fe and Fe$_2$O$_3$ with long organic alkyl chains having a functional group at their ends. In addition to the regular questions, such as organization of the alkyl chains, chemical bonding versus physical absorption, and thermal stability, a new dimension, that of magnetic properties, has been added. The question asked was whether by changing the functional group, or the alkyl chain, it is possible to ‘tailor’ the magnetic properties. The answer obtained was a positive one. The magnetic properties depend strongly on the nature of the functional group bonded to the Fe or to the Fe$_2$O$_3$ nanoparticles. For example, the saturation magnetization (in fact, saturation is not observed and is only an approximate number) of thiols, carboxylic acids, and alcohols bonded to Fe is about 50–80 emu/g Fe, whereas those having sulfonic and phosphonic acids are only 4–8 emu/g Fe. The comparison is made for chains with an equal number of carbon atoms. These differences are also reflected in the blocking temperatures of the coated particles.

Another closely related field that we have developed is the sonochemical coating of submicron ceramic spheres (silica, alumina, and zirconia) by a large variety of nanoparticles. This was done by synthesizing the ceramic spheres by conventional techniques (like the Stobbler method for silica particles). The spheres were then introduced into the sonication bath, mixed with the solution of the precursor, and ultrasonic radiation was passed through the solution for a predetermined time. In this way we were able to deposit on the surface of the ceramic spheres nanoparticles of metals (Ni and Co for example), metal oxides (Fe$_2$O$_3$, Mo$_2$O$_3$), rare earth oxides (Eu$_2$O$_3$, Tb$_2$O$_3$), semiconductors (CdS, ZnS), and Mo$_2$C. A figure presenting a bare silica sphere and a coated silica sphere is shown in Figure 1. The silica sphere is coated by nanocrystalline silver. Ultrasound irradiation of a slurry of silica submicrospheres, silver nitrate, and ammonia in an aqueous medium for 90 min, under an atmosphere of argon to hydrogen (95:5), yielded a silver–silica nanocomposite. By controlling the atmospheric and reaction conditions, we could achieve the deposition of metallic silver on the surface of the silica spheres.

Obtaining amorphous products is of importance in a number of fields of science, particularly in catalysis, where an amorphous nanoparticle is more active than the corresponding nanocrystalline particle having the same diameter. This was explained as being due to the dangling bonds active in the amorphous catalyst. Over the years, we have examined our products as catalysts in oxidation reactions, in the oxidation of cyclohexane. In a series of papers we compared the catalytic performance of sonochemically-made catalysts in this reaction.

In the last two years, we have concentrated our sonochemical efforts in two directions: sonochemical synthesis of mesoporous (MSP) materials, and the use of ultrasound radiation in the deposition of amorphous nanoparticles into the mesopores. We have developed a sonochemical method to prepare MSP silica, MSP titania, MSP YSZ (Yttria stabilized zirconia), and other MSP materials.

Figure 1. TEM image of silver nanoparticles deposited on silica spheres.
The sonochemical method is faster than the corresponding sol-gel preparation technique. The sonochemical products were shown to have thicker walls than those synthesized by the conventional methods. We have shown that the products are more hydrothermally stable than the sol–gel products. Our MSP titania has the highest surface area reported.

In addition, we have used sonochemistry for the insertion of amorphous nanoparticles into the mesopores. We have deposited Mo₂O₅ into the mesopores of MCM-41 (MSP silica)¹⁰, and amorphous Fe₂O₃ (ref. 11) into the mesopores of MSP titania. Five physical methods were used to prove that the amorphous nanoparticles were indeed anchored onto the inner walls of the channels. The amount of Mo₂O₅ that was inserted in the mesopores was 45% by weight. An attempt to increase this amount showed that the excess is deposited outside the mesopores. In a recent paper submitted for publication, we reported the synthesis of MSP iron oxide. Its catalytic activity in the oxidation of cyclohexane is the highest obtained so far. It converts 36% of cyclohexane to cyclohexanol and cyclohexanone (5:1 ratio) at 70°C and under one atmosphere of oxygen.

The second project is related to the sonochemical preparation of air-stable iron nanoparticles having a very high magnetization. Iron nanoparticles are pyrophoric and protecting them against oxidation is a challenge. In the process developed in our laboratory, we sonicated the solution of Fe(CO)₅ in diphenylmethane. The as-prepared material is composed of iron nanoparticles coated by a polymer. Further annealing of the sample yields an air-stable product¹². The characterization of the product and the stability studies are based on Mössbauer spectroscopy, XRD, and magnetization measurements.

Although some efforts in materials science are still directed towards developing new methods for the fabrication of nanomaterials, more attention is being directed presently to control of the size and shape of nanoparticles. We have demonstrated over the years that the control of the particle size is quite easy when using sonochemistry. It is accomplished simply by varying the concentration of the precursor in the irradiated solution. The more dilute the solution, the smaller the particles. The shapes of the products of the sonochemical process are less predictable. A major factor is the presence or absence of a surfactant.

We can just mention that shapes such as olympic nanorings (BaFe₂O₅) (ref. 13), nanocylinders (GaOOH) (ref. 14), nanotubes (TiO₂) (ref. 15), nested inorganic fullerenes (Ti₃O) (ref. 16), and spheres have been among the shapes of the sonochemical products. The inorganic fullerenes presented in Figure 2 were obtained as part of a study in which the sonohydrolysis of group III A (Ga, Al, In, and Tl) in the periodic table was conducted. An aqueous solution of the chlorides of these metals was sonicated at room temperature. The sonohydrolysis of TiCl₃ yielded onion-like nested fullerenes. They were assigned to Ti₃O which was one of the two sonication products.

We have demonstrated that the high temperature developed during the sonication was the driving force for the sonohydrolysis. Heating an aqueous solution of GaCl₃ for example, to 300°C, in a closed cell did not yield any product.

In addition to the catalytic applications mentioned above, the sonochemical products will be applied to two other fields. The first is their use as electrode building materials in rechargeable Li batteries, and the second is the fabrication of rare-earth doped optical fibers, which involves the sonochemical deposition of nanosized rare-earth oxide on the surface of submicron silica spheres.