SONOCHEMISTRY
and its Application in Materials Science

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We are all aware of the use of ultrasound radiation in medicine, where it is being used mostly for diagnosis, and more recently focused ultrasound radiation is being used to burn cancer cells. Less is known of its application in chemistry, despite the fact that it has applications across almost the whole breadth of chemistry. One of the main advantages in conducting sonochemical experiments is that it is very inexpensive to get started in the field. The current review is aimed at introducing the field of sonochemistry and describing the activities in our laboratory.

Let us first address the question of how 20kHz radiation can rupture chemical bonds, and try to explain the role of a few parameters in determining the yield of a sonochemical reaction, and what are the unique products obtained when ultrasound radiation is used in Materials Science. General introductions to the subject can be found in recent books and reviews [1-4].

A number of theories were developed in order to explain how a 20kHz sonic radiation can 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 to a distance of two van-der Waals radii, would require a power of 105 W/cm^2. On the other hand, it is well known that in a sonication bath, with a power of 0.3 W/cm^2, water is already converted to hydrogen peroxide. Different explanations were 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. The experimental evidence, that when the solution undergoes ultrafiltration, before the application of the ultrasonic power, there is no sonochemistry, supports these theories. The second stage is the growth of the bubble, which occurs through the diffusion of solute vapor to the volume of the bubble. The third stage is the collapse of the bubble that happens when the bubble size reaches its maximum value. According to the hot-spot mechanism, this implosive collapse raises the local temperature to 5000^{o}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 $Fe(CO)_5$ as a neat liquid, or its solution in decalin, yielded 5-20 nanometer size amorphous iron particles [5]. The reason for the amorphicity of the products is related to the high cooling rates (>10^{11} K/sec) 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 [6]. 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 importance. This is the interfacial region, which surrounds the collapsing bubble. Its width is calculated to be 200 nm, and the temperature reached after collapse 1900^{o}K [7]. 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 where 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. We will just mention one important parameter, the temperature. The equation of an adiabatic implosion is

$T_{max} = T_0 \{P_{ex}(g-1)/ P_{bub}\}$.

where T_{max} is the temperature reached after the collapse of the bubble, T_0 is the temperature of the sonication bath, $g=C_p/C_v$, P_{ex} is the external pressure equal to the sum of the hydrostatic and acoustic pressure, and P_{bub} 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 vapors of the solute can be found inside the cavitating bubble. Thus P_{bub} is practically the vapor pressure of the solute, and since it is found in the denominator, lower Pbub 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 were measured for sonochemical reactions.

Since 1996, when our first papers began to appear, we have published more than 100 papers describing the preparation of a large variety of nanomaterials, including metals, alloys, metal oxides, metal sulfides, metal nitrides, chalcagonides, 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. Here are 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_2O_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, the magnetic properties were 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 positive. The magnetic properties depend strongly on the nature of the functional group bonded to the Fe, or Fe_2O_3 nanoparticles. For example, the saturation magnetization (in fact saturation is not observed and it is only an approximate number) of thiols, carboxylic acids, and alcohols bonded to Fe are about 50-80 emu/gr Fe, whereas those having sulfonic and phosphonic acids are only 4-8 emu/gr 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 Stobber method for silica particles). The spheres were then introduced in the sonication bath, mixed with the solution of the precursor and the 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 sphere nanoparticles of metals (Ni and Co for example), metal oxides (Fe_2O_3, Mo_2O_5), rare earth oxides (Eu_2O_3, Tb_2O_3), semiconductors (CdS, ZnS) and Mo_2C. A figure presenting coated silica spheres is shown in Figure 1.

Obtaining amorphous products are of importance in a number of fields of science, in particular 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 an oxidation reaction, 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 concentrated our sonochemical efforts in two directions, sonochemical synthesis of mesoporous (MSP) materials, and the use of ultrasound radiation in the deposition of amorphous nanomaterials into the mesopores. We have developed a sonochemical method to prepare MSP silica [8], MSP titania [9], MSP YSZ (Yittria stabilized zirconia), and other MSP materials. 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 Mo_2O_5 into the mesopores of MCM-41 (MSP silica)[10], and amorphous Fe_2O_3 [11] in the mesopores of MSP titania. Five physical methods were used to prove that the amorphous nanoparticles are indeed anchored onto the inner walls of the channels. The amount of Mo_2O_5 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 cyclohaxnone (5:1 ratio) at 70^{o}C and 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 the air-stable product [12]. The characterization of the product and the stability studies are based on Mossbauer 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 directed these days to the control of the size and shape of the 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 the variation of the concentration of the precursor in the irradiated solution. The more dilute the solution, the smaller are 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 ($BaFe_{12}O_{19}$) [13], nanocylinders (GaOOH) [14], nanotubes (TiO_2) [15], nested inorganic fullerenes (Tl_2O) [16], and spheres were among the shapes of the sonochemical products.

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.

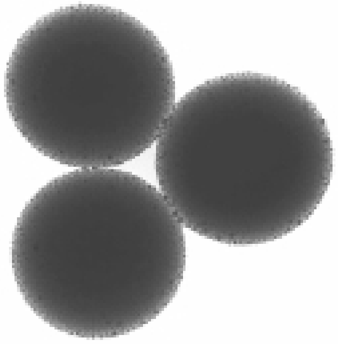

Figure 1. TEM image of silver nanoparticles deposited on silica spheres.

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Gedanken served as the Chairman of the Department of Chemistry and Dean of the Faculty of Sciences at Bar-Ilan University, and until recently he was the Chairman of the National committee for Advanced Materials and Chemical Technologies.