

Special tools in synthetic pathways of green chemistry: Electromagnetic Radiations

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Abstract: Scientists must design safer and cleaner approaches to manufacture the products needed by mankind. This approach can be proven only with the help of Green Chemistry. Green Chemistry can diminish the need for other approaches to environmental protection.

Keywords: Green Chemistry, ultrasonic wave, microwaves, nanoparticles

I. INTRODUCTION

The term “Green Chemistry” is defined as “the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances”. Green Chemistry can diminish the need for other approaches to environmental protection. Ideally, the application of green chemistry principles and practice renders regulation, control, clean up and remediation unnecessary, and the resultant environmental benefit can be expressed in terms of economic impact.

Green chemistry is an effort towards eliminating pollution by making chemical products that do not harm either our health or the environment and by using production processes that reduce or eliminate hazardous chemicals. Green chemistry prevents pollution at its source rather cleaning up the mess later. It is the high time that the chemists start thinking about the chemical process in the same way i.e. modification should be applied in the approach to achieve the result by following green pathway.

Green chemistry would like to increase the efficiency of synthetic methods, to use less toxic solvents, reduce the stages of the synthetic routes and minimize waste as far as practically possible. Prof Paul Anastas and Prof. John Warner have given the 12 principles for practicing green chemistry [1].

- A. Prevention of waste / by-products
- B. Atom Economy (maximum incorporation of the reactant into the final product)
- C. Prevention or minimisation of hazardous products
- D. Designing safer chemicals
- E. Design for energy efficiency
- F. Selection of appropriate solvents
- G. Use of renewable feedstock
- H. Reduce derivatives
- I. Catalysis
- J. Product obtained should be biodegradable
- K. Inherently safer chemistry for accident prevention
- L. Strengthening of analytical techniques to control hazardous compounds

II. APPLICATION OF MICROWAVES

The use of microwave radiation has become a widespread and convenient method for heating food and beverage in modern society due to the energy efficient and volumetric heated observed with microwave radiation. The use of microwave or dielectric heating in chemistry has been limited, however, with most applications occurring in organic chemistry. The fast and volumetric heating of organic reactions has lead to extraordinary reaction rate enhancements [2].

More recently the use of microwave radiation for heating reactions in the laboratory has expanded to inorganic and materials chemistry [3,4].

Microwaves are generated by a magnetron tube. Magnetrons were developed by Randall and Booth at the University of Birmingham during World War II [4]. These devices operate similar to a cathode ray tube, consisting of a heated cathode, a voltage biased anode, a magnetic field, and an antenna.

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Synthesis of Peptide bond synthesis was performed on PEGA (cross-linked acrylamide and polyethylene glycol) beads under microwave radiations. Classical chemical coupling as well as thermolysin catalyzed synthesis was studied, and the effect of microwave radiations on reaction kinetics, beads' integrity, and enzyme activity was assessed. Results demonstrate that microwave radiations can be profitably exploited to improve reaction kinetics in solid phase peptide synthesis when both chemical and biocatalytic strategies are used.

PEG is applicable to both chemical and enzymatic peptide synthesis under microwave irradiation. The benefit of MW radiation in terms of improvement of reaction kinetics has been demonstrated both in the chemical and enzymatic coupling. In the case of enzymatic coupling an optimum temperature of 80°C allows to achieve maximum reaction rates while avoiding the fast enzyme denaturation observable at higher temperature. : Synthesis of Fmoc-Phe-Phe-PEG under microwave radiation via enzymatic and chemical coupling. (a) (i) DIC/DMAP in DMF; (ii) Pyp 20%. (b) Chemical coupling (DIC/HOBt in DMF) or enzymatic coupling (Thermolysin in aqueous buffer) [5-7].

There are several common misconceptions associated with microwave radiation. They are that microwave radiation is energetic enough to directly affect chemical reactions; heats matter by rotating molecules, and can cause non-thermal reaction rate enhancements. Looking at the energy of microwave radiation in Table 1, one can see microwaves lack the energy to affect any common chemical bond. The actual mechanism of microwave heating does involve molecular rotational energy induced by microwaves, but intermolecular collisions occur on the same time scale in liquid phases, approximately every 10^{-30} seconds. These collisions prevent any full molecular rotation, and the rotational energy induced by the microwave radiation is converted into vibrational and translational energy. Other heating mechanisms, such as conductive and interfacial polarization, are present in solids under dielectric heating [5]. These are the primary mechanisms of heating with microwave radiation. Measuring the temperature of a reaction being heated with microwaves can be challenging, because the device used to measure the temperature can be affected by the radiation. All reaction rate enhancements have been shown to be thermally induced, in spite of claims to the contrary [8].

Table 1: Energy associated with microwave radiation and different chemical bonds

	Microwave Radiation	Brownian Motion	Hydrogen Bonds	Covalent Bonds	Ionic Bonds
Energy (eV)	10^{-6} to 10^{-4}	0.026 (298 K)	0.04 to 0.44	4.51 (C-H) 3.83 (C-C)	7.6

One of the earliest applications of microwave radiation to the synthesis of inorganic compounds was performed by Frazer and Holzmann followed quickly by Shriver and Jolly [9]. Frazer and Holzmann's work centered on the reductive dimerization of BCl_3 to B_2Cl_4 , while Shriver and Jolly observed the transformation of GeCl_4 to Ge_2Cl_6 under microwave radiation.

Continuing this early application of microwaves, Mingos and his co-workers [10] expanded the application of microwave heating to solid state reactions. During their investigation it was observed that some metal oxides were sensitive to dielectric heating. Copper (I) oxide reached 550 °C after irradiation for 1 minute at 500 W. WO_3 and V_2O_5 heated to >700 °C under the same conditions, and melted upon further heating.10 By applying these observations, Mingos and his co-workers were able to synthesize high-Tc superconducting oxides La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. [11]. This early work showed the utility of microwave radiation in the synthesis of inorganic compounds and materials due to the time and energy savings observed.

From these early applications microwave radiation has been applied to the synthesis of modern, advanced materials such as nano-materials, thin films, and porous ceramics [12-14]. There has been intense interest in the development of nano-materials because of their size dependent properties stemming from varying degrees of quantum confinement of the electrons in the material. El-Shall and his co-workers have developed a microwave-assisted synthesis for one dimensional cadmium and zinc chalcogenide rods and wires [15]. Their microwave process produced aligned, ultra narrow nano rods and nano wires. The fast and volumetric dielectric heating from microwaves made their synthesis very fast, and produced uniform materials.

The development of thin films is an important area of materials chemistry that has a large impact on the microelectronics industry. There are many methods for depositing thin films, and the morphology of the film is highly dependent on the method of deposition. In particular, Hui Yan and co-workers have shown that thin films of zinc and cadmium sulphide can be controllably deposited on glass substrates [16]. In addition, Richard Masel and co-workers have developed a novel method for the chemical vapour deposition

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of Ta₂O₅ utilizing microwave heating to produce the chemical vapour [17]. The microwave deposition of these films is advantageous because it does not require expensive high vacuum chambers, nor are these methods limited to slow deposition rates. Finally, porous materials have become important in chemistry due to their catalytic and gas storage abilities. Historically, zeolites have found widespread usage [18], but more recently metal-organic frameworks (MOFs) have come a useful analogue. A significant drawback to these materials is the energy and time intensive processes required for their synthesis. In the early 1990's for zeolites [19] and just recently for MOFs, microwave heating has been shown to dramatically increase the rate of formation of these materials [20]. Microwave method has been proved to be a successful method in synthesis of various compounds, synthesis of ceramic products, polymer chemistry etc [21].

Sound waves with frequencies higher than those can be heard by human (>16 kHz) is called ultrasound. The upper limit of ultrasonic frequency is not sharply defined. It is usually taken to be 5 MHz for gases and 500 MHz for liquids and solids [22].

Use of sonication energy provides a better way to reach higher efficiency, higher rates for chemical, physical, or physico-chemical process, shorter processing times and change reaction pathways. Knowledge on mechanism of ultrasound provides a way to investigate some of fundamental properties of materials. An understanding of mechanisms for different (chemical, physical, biological) effects of sound is important in connection with its applications in different fields (medicine, food, chemistry). Knowledge on mechanisms of ultrasound is essential because of practical applications. There is considerable need to increase understanding of mechanisms in order to evaluate performances and limitations involved in its various applications.

This study describes mode of actions for ultrasound versus input energy. This work also provides different views and explanations on the mechanisms of ultrasound irradiation as a function of input energy with particular attention in the field of polymer degradation and food applications.

III. APPLICATIONS OF ULTRASOUND

Ultrasound with power levels of milli-watts (mW) or below is used industrially for measuring material proper-ties as a non-destructive, non-invasive testing and diagnostic technique [23-25]. It is used in many fields of science, engineering, food and medicine. Characterization of materials by ultrasound has advantages over many of traditional techniques: it is capable of rapid and precise measurements. It is used to characterize fats and oils (dynamic rheology and composition of oils, oil con-tent, droplet size of emulsions and the solid fat content of partially) [24]. Low intensity ultrasound is a powerful analytical technique for investigating physico-chemical properties of many biological and non-biological materials. High frequency (>1 MHz) with low intensity waves are useful in providing information on relaxation phenomena such as segmental motion, conformational analysis, vibrational - translational energy inter-charge and polymer solvent interactions [26].

The use of low frequency with sufficiently high power of ultrasound in industrial processes has two main requirements; a liquid medium (even if the liquid forms only 5% of the overall medium) and a source of high- energy vibrations (the ultrasound). Low frequency with sufficiently high power of ultrasound has been employed a wide variety of industries as follows: cleaning, sterilization, floatation, drying, degassing, defoaming, filtration, homogenization, emulsification, dissolution, de- aggregation of powder, biological cell disruption, extraction, crystallization, chemical processes, acceleration of chemical processes, organic synthesis, and provide in-formation on both polymerization and partial depolymerization and preparation of moderate macromolecules from large ones [23,27-37]. Applications of ultrasonic irradiation versus input power is given in **Table 2**.

Table 2. Applications of ultrasonic irradiation versus input power.

Input Power	Low energy	High energy
Performances/ characteristics	Non-destructive; non-invasive testing; diagnostic technique; to measure material properties.	To perform various (chemical, biochemical and biochemical) processes; to accelerate various processes.
Food applications	To determine physico-chemical properties and characterization of food and biological components.	Sterilization, drying, defoaming, filtration, homogenization, emulsification, dissolution, de-aggregation of powder, biological cell disruption, extraction, crystallization, acceleration of several processes.
Polymer applications	To provide information on segmental motion and polymer- solvent interactions; to determine polymer conformation.	Polymerization, fragmentation, depolymerization, acceleration of polymer synthesis and depolymerization.

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Nano structured metals were first prepared in non-aqueous solutions. Suslick and coworkers have developed a novel route to prepare nano structured amorphous iron metal (Figure 1a) and colloidal iron nano particles (Figure 1b) [38-40]. Highly volatile iron pentacarbonyl decomposes into iron atoms during sonication, and depending on the presence of an organic or polymeric stabilizer, either agglomerates of nanoparticles or colloidal nanoparticles are obtained. Stabilizers (e.g., oleic acid or polyvinyl-pyrrolidone) can trap the sonochemically decomposed iron nano clusters before aggregation, resulting in colloidal nanoparticles. The amorphous iron metal powder has a high surface area of $\sim 150 \text{ m}^2 \text{ g}^{-1}$, owing to its porous and coral-like structure, and the sonochemically prepared colloidal iron nanoparticles show narrow size distributions centered at $\sim 8 \text{ nm}$ and are found to be super paramagnetic. The amorphous nature of sonochemically prepared iron results from the enormously fast cooling rates of hot spots during acoustic cavitation (i.e., solidification precedes crystallization).

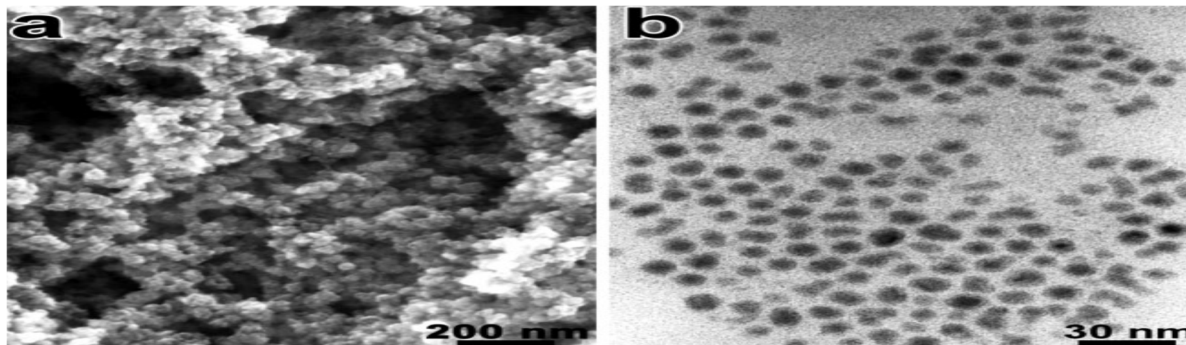


Figure 1 . Sonochemically prepared a) amorphous iron (reproduced with permission from [43], and b) iron colloid (reproduced with permission from [40])

Another shape control method using ultrasound was reported by Liz-Marzán and co-workers [41-42]. They synthesized monodispersed gold nano decahedra with high yield and noticeably increased reproducibility via ultrasound-induced reduction of HAuCl_4 on pre-synthesized gold seeds in N,N -dimethyl formamide (DMF) solution. Surprisingly, thermal reduction without the use of ultrasound produces a lower yield of gold decahedra with increased polydispersity. A similar synthetic strategy was exploited by Zhu and colleagues in the synthesis of silver nanoplates [43]. In their synthesis, the ultrasound-assisted Ostwald ripening process leads to the growth of silver nanoplates from silver nano particles formed at an early stage of reaction.

IV. ADVANTAGES

Microwave is simple, convenient, fast, high yielding, efficient and environment friendly synthetic methodology [44]. Microwave synthesis is considered as a “Green Technology” principally since many organic reactions can be carried out in solvent – free conditions. Microwave radiation has proved to be a highly effective heating source in chemical reactions.

Microwave can accelerate the reaction rate, provide better yields and uniform and selective heating, achieve greater reproducibility of reactions and help in developing cleaner synthetic techniques.

Practically in all reports, main attention of researchers is paid to extreme fastness of MW assisted reactions in comparison with classic protocols. The same reactions in the MW- yield take place in 10-100 times more rapidly. Moreover, higher or comparable yields are frequently reported. Sometimes the MW – route leads to products, which it is impossible to get via traditional pathways, for instance preparation of several metal cluster complexes [45]. Sonochemistry is one of the green chemistry research area in which molecules undergo a reaction due to the application of powerful ultrasonic radiation. The ultrasound irradiation is a powerful technique for establishing unique chemical and physical conditions, such as a local increase in temperature of several thousands of Kelvins and pressure by several bars by which reaction proceeds [46].

V. DISADVANTAGES

Temperature measurement especially for the reaction in dense and solvent-less medium is difficult. Heating microwave cavities is based upon the ability of some liquid and solids to absorb and transform electromagnetic energy into heat. When a strongly conducting material is exposed to microwave irradiation, Microwaves are largely reflected from its surface. So, the material is not effectively heated by microwaves, in response to the electric field of microwave radiation, electrons move freely on the surface of the material, and the flow of electrons can heat the material through a resistive heating mechanism. While in the case of insulator

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microwave radiation can penetrate through the material without any absorption, loss or heat generation. They are transparent to microwave. Passage of microwave which is electromagnetic in nature can give rise to absorption of microwave energy and heat generation due to the so called dielectric heating mechanism.

Heat force control is difficult. Water evaporation occurs. There for its applications have been limited to small scales use in labs and have not been extended to production level [47].

In ultrasonic synthesis changes in the environment, such temperature, pressure, humidity, air turbulence and airborne particles affect ultrasonic response.

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