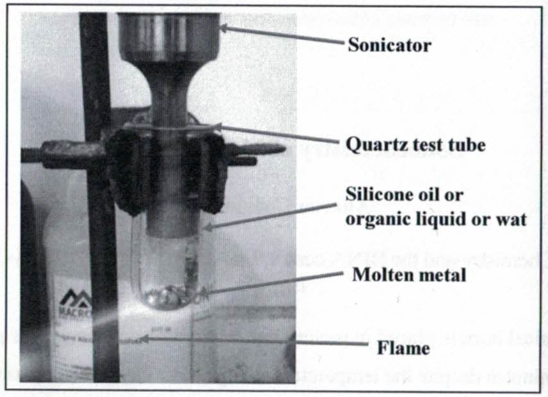

Figure 1. A simple scheme of conducting sonochmistry of molten metals

Role of the solvent in US-assisted preparation of TiO$_2$ for the photocatalytic degradation of Sulfamethoxazole in water

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Powered TiO$_2$, with crystallites always in the range of nanometers, was synthetized using ultrasound during the sol-gel process, in different solvents. The advantages of ultrasonication method are demonstrated as compared to the conventional stirring method of preparation of titania [1]. Sonochemical process to obtain materials with improved or unusual properties is an alternative to traditional TiO$_2$ synthesis procedure, i.e. sol-gel method, hydrothermal technique, reverse micelle method or oxidation of metallic Ti powder. Ultrasound (US) assisted synthesis of titanium dioxide is well known in recent literature. The chemical effect of US arises from acoustic cavitation, i.e. the formation, growth and implosive collapse of bubbles in a liquid. An interesting feature resulting from the application of sonication as a synthetic method is the production of nanoparticles showing a more uniform size distribution, higher surface area and a more controlled phase composition.

The influence of ultrasound during the preparation of photoactive TiO$_2$ was here investigated optimizing the growth of the crystallites size: in particular, we observe a modification of the material properties modifying the solvent used during the preparation (Fig. 1). Five different organic solvents were chosen for the present study: n- hexane, decane, isopropanol, ethanol and 1-octanol. After the synthesis powders were characterized by FE-SEM, TEM, BET, XRD and Micro Raman. The powders obtained have been tested in the photodegradation of sulfomethoxazole (SMX), that is most common antibiotic, a very resistant molecule that passes fully undegraded through the common purification plants. Besides being used for human therapy, antibiotics are extensively used for animal farming and for agricultural purposes. Residues from human environments and from farms may contain antibiotics and antibiotic resistance genes that can contaminate natural environments.
To try to solve this fact, Advanced Oxidation Processes seem to give very satisfactory answers. In particular, photocatalysis is a very efficient process, which often allows the complete degradation of the pollutant molecules without the aim of new reactants like Fenton-process, for example.

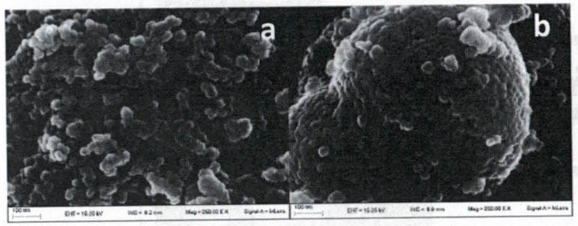

Figure 1. FE-SEM images of TiO_2 synthetized with ultrasound in two different solvents: a) Hexane b) Isopropanol

Degradation results adding TiO_2 show a common trend: samples prepared via US are always more active than the corresponding TiO_2 prepared under common hydrolysis confirming the importance of US during the preparation (Fig.2). Moreover, polar solvents lead to better photocatalysts confirming that the presence of both pure anatase and good surface area are usually the best constituents for a photoactive material.

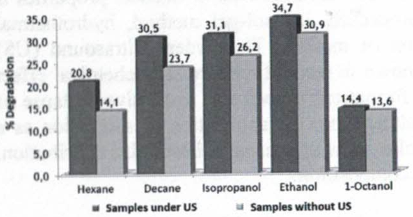

Figure 2. Degradation of SMX after 6 h in different TiO_2 synthetized with different solvents

[1] C.Y. Teh et al., *Chemical Engineering Journal,* 317 : 586–612. **2017**

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Sonochemically Produced Hollow Polymer Microspheres for Temperature Responsive Delivery

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Since the pioneering work of Suslick and Grinstaff,[1] a number of workers have demonstrated that hollow protein microspheres can be rapidly and conveniently prepared using ultrasound. Hydrophobic species dissolved in e.g. tetradecane can be encapsulated e.g. as contrast agents or drug delivery agents. Ashokkumar and co-workers have used similar methodology [2] to prepare microspheres from synthetic polymers based on thiolated poly(methacrylic acid), PMASH.

We have demonstrated [3] the feasibility of encapsulating hydrophilic species by dissolving them in the aqueous phase of an water-in-oil emulsion (also produced sonochemically) and encapsulating this emulsion in lysozyme or poly(methacrylic acid) microspheres (Figure 1). A combination of a water soluble green dye (fluorescein) with a red dye compatible with the organic phase (Nile Red) allows us to image both the phases within a microsphere. We can release the contents chemically (using DTT to break the crosslinks) or mechanically (using 20 kHz ultrasound) by rupturing the wall of the microspheres. Components other than hydrocarbon oils can be used to form the emulsions.

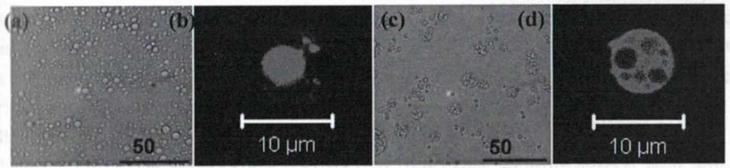

Figure 1. (a) Optical micrograph and (b) LSCM image of nile red in tetradecane filled PMASH microspheres, (c) optical micrograph and (d) LSCM image of emulsion filled PMASH microspheres.

We are interested in developing delivery systems that respond to their environment. In this direction, we have developed several block copolymers based on PMASH which can sonochemically form microspheres. One block is responsive to external stimuli, for example pH and/or temperature. Using poly(NIPAM), allows us to trigger release around body temperature as shown in Figure 2. We can also incorporate magnetic materials and/or noble metal nanoparticles (also produced sonochemically) into the shell.

In addition to varying the shell materials, we can vary the materials incorporated into the microspheres. A range of natural oils have been used which means that the microspheres can be used, for example, in sustainable agricultural applications.