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Hybrid/porous materials obtained from nano-emulsions

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ABSTRACT

Nano-emulsions known also as mini-emulsions, ultrafine emulsions or submicron emulsions are a specific kind of emulsions that have a sub-micrometer droplet size and a low polydispersity. Nano-emulsions, being kinetically stable systems, require energy input in order to be formed, either from mechanical devices or from the intrinsic physicochemical potential of the components. The properties of the nano-emulsions make them suitable for applications in various domains such as drug delivery, cosmetics, pesticides and in particular for the preparation of inorganic or hybrid nanostructured materials. This review discusses the recent progresses made in this latest field. We focus on inorganic or hybrid nanoparticles, nanocapsules, hollow spheres or composites prepared by combining the nano-emulsion technique and the sol–gel process. In that case nano-emulsions act as template. We also outline the most recent development, which consists in using the nano-emulsions as imprints to get hierarchical porous silica materials.

1. Introduction

Inorganic and hybrid porous materials are of particular interest, for example in the preparation of catalysts, drug delivery systems or sensors [1–3]. Their expansion is due to the development of soft chemical processes, such as sol–gel chemistry. One approach to prepare these compounds consists in using surfactant-based systems to induce the porosity. For example ordered mesoporous materials can be synthesized by using micelles or liquid crystals through the cooperative or the liquid crystal templating mechanism, respectively. These mesostructured materials can be functionalized to tune their surface properties [4]. Both post synthesis grafting of an organic compound, such as an organoalkoxysilane, on a substrate or co-hydrolysis and polycondensation of an alkoxysilane, for instance tetramethylorthosilicate (TMOS), and an organoalkoxysilane result in the material functionalization [5]. However, the limited diffusion within substrates through confined nano-channels can be a problem for practical applications such as in catalysis [6]. The development of hierarchical pore structures at different length scales has therefore attracted much attention and the synthesis of micro-meso, meso-meso or macro-mesoporous materials has been investigated by different groups. Among the various templates such as latex spheres, solid lipid nanoparticles…, emulsions have been widely considered to create the macropore network [7,8]. Indeed, emulsion templating is a versatile method for the preparation of well defined open porous monoliths. In general, this technique involves the polymerization of the continuous phase and subsequent removal of the dispersed droplets by drying and heat treatment. It has been used to produce macroporous titania, silica and zirconia with pore sizes from 50 nm to several micrometers [8]. Another interesting strategy to prepare the porous materials deals with nano-emulsions. Nano-emulsions known also as mini-emulsions, ultrafine emulsions or submicron emulsions are a specific kind of emulsions that have a sub-micrometer droplet size and a low polydispersity. Generally the droplets of a nano-emulsion have a size smaller than 200 nm [9,10]. Due to their characteristic size, nano-emulsions have a transparent, bluish or reddish aspect and are extremely stable against sedimentation or creaming because it is prevented by the Brownian motion of their droplets. Due to their properties these systems are used for different kinds of applications [11–13]. For example in the pharmaceutics field, nano-emulsions emerge as a promising drug delivery technique [14]. Indeed, their mechanical, optical properties and droplet size can be controlled. For oil in water systems, many water insoluble drug molecules can be incorporated into the droplets, and their small size gives them the advantage of penetrating deep into tissues, thus fulfilling the criteria of many drug administration routes. Another promising application that may be considered for nano-emulsions is their use to prepare inorganic and/or hybrid porous materials with controlled texture through the sol–gel process. In that case the nano-emulsions act as templates, for example for the synthesis of

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nanoparticles or nanocapsules [15]. The main advantage is that each droplet can be considered as a single nanoreactor, allowing the control of the particle's dimension in the nanometer or submicrometer range by varying the size of the droplet. As regards the materials' preparation, another approach, which is barely reported, consists in using the nano-emulsions as a true imprint to create macropores in the nanometer range and combining a nano-emulsion templating mechanism with the self assembly one, hierarchical porous materials can be obtained. This review focuses on the two aspects mentioned above for using nano-emulsions to prepare porous and/or hybrid materials. A special zoom is given on papers recently published, mainly during the period between 2010 and 2016, which associate nano-emulsions with the sol–gel process to get these materials.

2. Nano-emulsion formulation

Nano-emulsions are kinetically stable dispersions and the droplets are usually formed by shear induced rupturing. An important shear rate is needed; high shear stirrers or high pressure homogenizers are sometimes not enough efficient. It is better to produce the nano-emulsions with high-frequency ultrasonic devices or microfluidic devices. Another way to get nano-emulsions, in particular from nonionic surfactant systems deals with the low energy methods, which are based on the physico-chemical properties of the system. In that case only a low quantity of energy is required to form the nano-emulsions since the emulsification is achieved thanks to the internal chemical energy of the system. Since the early 2000s, the number of publications dedicated to these low energy emulsification methods has strongly increased [16]. Most of the papers deal with the preparation conditions, the formulation, the physico-chemical properties and the structure of the nano-emulsions as well as the understanding of their formation mechanisms. The Solans' group [9] has widely contributed to the enthusiasm for this topic by developing low energy methods taking benefit from the knowledge acquired a long time ago by Shinoda and Frieberg on the nonionic surfactants systems [17]. Since then, progresses concerning the understanding of these systems have been made thanks to the development of the experimental techniques and in particular in the microscopy field. Several reviews concerning the formulation and the preparation of nano-emulsions have been published [9,18,19]. In the category of low-energy emulsification process, different methods are distinguished in the literature and according to the authors the classification can vary. Excess of rationalization is not always adapted, especially as some contradictions can be found in the description of the emulsification mechanisms. From our point of view, even if now there is a better control of emulsions, some gray areas still exist in the case of the nano-emulsions formation. Especially as with the various investigated systems, the ways to get them have been multiplied. It should be noted that contrary to microemulsions, which are thermodynamically stable systems, the formation of nano-emulsions can be sensitive to several parameters such as the order of component addition, the stirring rates, the nature and the number of phase transitions and so on. The most common low-energy methods are those based on phase inversion (phase inversion temperature method, PIT, or phase inversion composition method, PIC, and the so-called self-emulsification methods), that are usually based on dilution and/or diffusion processes. They will be briefly described below.

2.1. Emulsification by PIT method

This terminology comes from H. Saito and K. Shinoda, who have investigated, in 1969, the stability and the characteristics of emulsions as a function of both the temperature and of the surfactant HLB value [20]. This process consists in mixing water, oil and surfactant and then the temperature of the mixture is quickly increased near the PIT. A fine emulsion (nano-emulsion) can be easily obtained due to the fact that at this temperature the interfacial tension is low. In return, the emulsion can degrade quickly by coalescence. To avoid this phenomenon the system is quenched by cooling it at a temperature situated at around 20 °C below the PIT. However, this shift in temperature depends on the investigated system. The stability of the nano-emulsion and the droplets size are affected by the temperature at which the samples are heated. If this temperature is higher than the PIT, water droplets in oil are obtained and during the cooling oil in water nano-emulsions are formed according to a true phase inversion. By contrast if the temperature is a little below the PIT, an oil in water emulsion is directly obtained. Finally if the sample is placed at the PIT a single phase bicontinuous microemulsion is present when the surfactant is well defined. When a technical grade surfactant was used the bicontinuous microemulsion was in equilibrium with another phase (lamellar or water) and in that case, nano-emulsions with smaller-size droplets were formed [19,21].

2.2. Emulsification by PIC method

This term is used by C. Solans [22] to distinguish this emulsification process operating at constant temperature from the one described above where the emulsification is induced by a change in the temperature. In the case of O/W nano-emulsions, for a given oil over surfactant ratio, water is progressively added under stirring to an oil-surfactant mixture. At the beginning the system is usually a reverse micellar solution. Upon the progressive addition of water phase transitions can take place and the phase inversion is triggered after the detection of a bicontinuous and/or a lamellar phase. The water addition allows the formation of small oil droplets in water, which can be the diluted to obtain the nano-emulsions. This method is easy to perform and by comparison with the emulsification by the PIT, the number of the experimental parameters that should be considered is reduced.

2.3. Self emulsification method

Under this label are gathered the methods allowing the emulsification process without phase inversion and usually at constant temperature [9]. They are also designed as spontaneous emulsification. In the literature the “Ouzo effect” [23], which depicts quite well the spontaneous phenomenon, is often described. This effect is generated by the rapid diffusion of a water-miscible solvent, such as ethanol, solubilized first in the oily phase. Then it moves quickly to the aqueous phase, when the two phases are in contact very small oil droplets are generated. This kind of system is very stable and does not necessary contain a surfactant. A similar behavior has been evidenced for other systems. For example, the dilution of O/W microemulsion containing ionic surfactant and co-surfactant can induce the formation of O/W nano-emulsions by the migration of the co-surfactant to the aqueous phase [24]. The composition of the microemulsion interfacial film is modified when water is added. This involves a destabilization of the microemulsion and as a consequence an O/W emulsion with very fine droplets is formed. This scenario is not restricted to microemulsions; direct cubic liquid crystal phases also lead to the formation of O/W nano-emulsions by dilution [25].

However, to make use of these low-energy approaches, it is necessary to know in detail the phase behavior of the considered surfactant/oil/water system.

3. Silica hybrid/porous materials

The kinetic stability of nano-emulsions and their transparent or translucent appearance make these systems interesting for the preparation of nanostructured materials. In particular the so-called “nano-emulsion technique” [26,27,28] has been used to synthesize organic, inorganic or hybrid nanoparticles, nanocapsules and microspheres. Among the different materials silica is of peculiar interest. Indeed, for example, silica nanoparticles have promising developments in biological fields for bioimaging, diagnosis, controlled drug- or DNA-delivery