9

New Trends on the Synthesis of Inorganic Nanoparticles Using Microemulsions as Confined Reaction Media

Margarita Sanchez-Dominguez[1], Carolina Aubery[2] and Conxita Solans[2]
[1]Centro de Investigación en Materiales Avanzados, S. C. (CIMAV), Unidad Monterrey;
GENES-Group of Embedded Nanomaterials for Energy Scavenging
[2]Instituto de Química Avanzada de Cataluña, Consejo Superior de Investigaciones Científicas (IQAC-CSIC); CIBER en Biotecnología, Biomateriales y Nanomedicina (CIBER-BBN)
[1]Mexico
[2]Spain

1. Introduction

The development of nanotechnology depends strongly on the advances in nanoparticle preparation. Nowadays, there are a number of technologies available for nanoparticle synthesis, from the gas phase techniques such as laser evaporation (Gaertner & Lydtin, 1994), sputtering, laser pyrolisis, flame atomization and flame spray pyrolisis (Kruis et al. 1998), etc, to the liquid phase techniques such as coprecipitation from homogeneous solutions and sol-gel reactions (Qiao et al. 2011), solvothermal processes (Gautam et al. 2002), sonochemical and cavitation processing (Suslick et al. 1996), and surfactant and polymer-templated synthesis (Holmberg, 2004). Amongst the surfactant-based approaches, the microemulsion reaction method is one of the most used techniques for the preparation of very small and nearly monodispersed nanoparticles. This method offers a series of advantages with respect to other methods, namely, the use of simple equipment, the possibility to prepare a great variety of materials with a high degree of particle size and composition control, the formation of nanoparticles with often crystalline structure and high specific surface area, and the use of soft conditions of synthesis, near ambient temperature and pressure. The traditional method is based on water-in-oil microemulsions (W/O), and it has been used for the preparation of metallic and other inorganic nanoparticles since the beginning of the 1980's (Boutonnet et al., 1982). The droplets of W/O microemulsions are conceived as tiny compartments or "nanoreactors". The main strategy for the synthesis of nanoparticles in W/O microemulsions consists in mixing two microemulsions, one containing the metallic precursor and another one the precipitating agent. Upon mixing, both reactants will contact each other due to droplets collisions and coalescence, and they will react to form precipitates of nanometric size (Figure 1). This precipitate will be confined to the interior of microemulsion droplets. Numerous investigations have been published about the use of W/O microemulsions for the preparation of a variety of nanomaterials, such as metallic and bimetallic nanoparticles, single metal oxide as well as mixed oxides, quantum dots, and even complex ceramic materials (Boutonnet et al., 1982; Destrée & Nagy, 2006; Eastoe et al. 2006; Holmberg, 2004; López-Quintela et al. 2004; Pileni 1997 and 2003). Materials synthesized in w/o microemulsions exhibit unique surface properties; for example, nano-catalysts prepared by this method show better performance (activity, selectivity) than those prepared by other methods (Boutonnet et al. 2008).

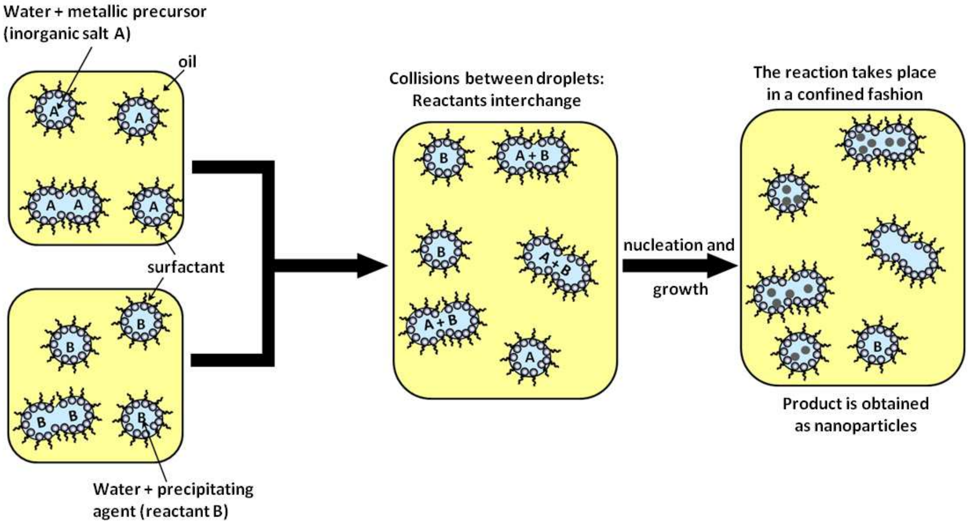


Fig. 1. Scheme of the w/o microemulsion reaction method for the synthesis of inorganic nanoparticles.

In spite of the superior properties and performance of nanoparticles obtained in w/o microemulsions, this method has not found good acceptance at the industrial level, mainly due to the employment of large amounts of oils (solvents) which represent the continuous and hence main component of these systems. In addition, most studies employ relatively low concentration of the metal precursors, leading to small yields of nanoparticles per microemulsion volume. These drawbacks affect negatively from the economic and ecologic point of view. It is the aim of this chapter to review the newest trends in the synthesis of inorganic nanoparticles using microemulsions as confined reaction media, with the objective to identify those alternatives or approaches that make this type of colloidal media more attractive for nanoparticle synthesis from the environmental , economic, technological, and scientific point of view. Some of those approaches are: the synthesis of advanced materials, such as mixed oxides and complex ceramics with nanocrystalline structure, core-shell particles, mixed materials with key nano-heterojunctions, etc, which may be difficult to obtain by other methods; optimization of microemulsion compositions, by making use of advanced phase behaviour knowledge; use of bicontinuous microemulsions in semi-continuous batches, and last but not least, a novel approach based on the use of oil-in-water microemulsions instead of w/o microemulsions as confined reaction media. An introductory section about the generalities and properties of microemulsion systems as well as on the use of microemulsions as reaction media for nanoparticle synthesis is first included. In addition, other aspects of nanoparticle synthesis are reviewed, such as study of reaction kinetics; influence of microemulsion dynamics on the characteristics of the obtained materials, as well as phase-transfer and isolation of nanoparticles from the microemulsion reaction media.

2. General properties and formation of microemulsions

2.1 Microemulsions: Definition and basic properties

Microemulsions are transparent and thermodynamically stable colloidal dispersions in which two liquids initially immiscible (typically water and oil) coexist in one phase due to the presence of a monolayer of surfactant molecules with balanced hydrophilic-lipophilic properties (Danielsson & Lindman, 1981). They are optically isotropic and transparent. In contrast to emulsions, for which formation requires a considerable energy input, microemulsions form spontaneously upon gentle components mixing, once composition and temperature conditions are right. Depending on the ratio of oil and water and on the hydrophilic-lipophilic balance (HLB) of the surfactant, microemulsions can exist as oil-swollen micelles dispersed in water (oil-in-water microemulsions, O/W), or water-swollen inverse micelles dispersed in oil (water-in-oil microemulsions, W/O); at intermediate compositions and HLBs, bicontinuous structures can exist. When a dispersed phase is present, it consists of droplets with a narrow size distribution in the order of 2-50 nm.

The formation of microemulsion depends on the surfactant type and structure, e.g. single hydrocarbon chain ionic surfactants require the incorporation of cosurfactant or electrolytes for microemulsion formation due to their high hydrophilic character; in contrast, double chain ionic surfactants and ethoxylated non-ionic surfactants may form microemulsions without cosurfactant. Lowering the interfacial tension between the oily and aqueous phase ($\gamma_{o/w}$) is the main role of the surfactant (or surfactant/cosurfactant mixture). The extremely low $\gamma_{o/w}$ (in the order of 10^{-2} - 10^{-3} mN m^{-1}) achieved is one of the main microemulsion characteristics: the decrease on $\gamma_{o/w}$ is caused by the surfactant, overcoming the surface energy term caused by the huge increase in interfacial area. In addition, the spontaneous dispersion of numerous water or oil droplets causes an entropy increase, yielding a thermodynamically stable system. The extremely low interfacial tension is decisive for microemulsion formation, and depends on the composition of the system (Kunieda & Friberg, 1981; Cross, 1987).

Microemulsions are dynamic systems, and it has been shown that droplet content exchange processes can occur in the order of millisecond time scales (Fletcher et al., 1987; Clarke et al., 1990). Collisions are produced due to constant Brownian motion of the droplets. When these collisions are sufficiently violent, the surfactant layer breaks up and the micellar exchange can be produced. It is thought that the micellar exchange process is characterized by an activation energy (E_a or energy barrier), which is affected by the flexibility or rigidity of the surfactant layer (Fletcher & Horsup, 1992; Lindman & Friberg, 1999}, in addition to diffusion processes (Fletcher et al., 1987).

2.2 Microemulsions and phase equilibria

Phase behavior studies by means of equilibrium phase diagrams of polar solvent/amphiphile/nonpolar solvent systems provide essential information on microemulsion formation and structure. In 1954, Winsor predicted four types of equilibria which was latter experimentally evidenced: i) Winsor I: oil-in-water (o/w) microemulsions are formed, and the surfactant-rich water phase coexists with the oil phase where surfactant is only present as monomers; ii) Winsor II: water-in-oil (w/o) microemulsions are formed and the surfactant-rich oil phase coexists with the surfactant-poor aqueous phase; iii) Winsor III (middle phase): a three-phase system where a bicontinuous middle-phase microemulsion (rich in surfactant) coexists with both excess water and oil phases; and iv) Winsor IV: a single-phase (isotropic) micellar solution (microemulsion), that forms upon addition of a sufficient quantity of amphiphile. Figure 2 shows how this equilibria can be affected by salinity (for ionic surfactants) or temperature (for non-ionic surfactants), and also illustrates the structural variability of microemulsions (O/W, W/O and bicontinuous (BC)).

Some typical equilibrium phase diagrams are shown in Figure 3 (Destrée & Nagy, 2006). In each of these diagrams L_2 denotes a region where one phase W/O microemulsions are formed. AOT (Sodium 2-ethylhexylsulfosuccinate) based systems are amongst the best characterized systems, and it has been found that the size of the inverse microemulsion droplets formed by this type of systems increases linearly with the amount of water added to the system (Pileni, 1998) and can increase from 4 nm to 18 nm with 0.1 M sodium AOT surfactant (water/AOT/isooctane). AOT based systems are probably the most used for the synthesis of inorganic nanoparticles in w/o microemulsions, for two reasons: good control of droplet size as explained above and the large microemulsion regions found in water/AOT/alkane systems, which give rise to a great deal of compositions available for nanoparticle synthesis. Systems based on cetyltrimethylammonium bromide (CTAB), usually combine this surfactant with alcohols such as hexanol as the oil phase. This alcohol can act as co-surfactant, adsorbing at the oil/water interface along with the surfactant. As shown in Figure 3 the microemulsion region of water/CTAB/hexanol system is relatively narrow, however, when shorter alcohols such as butanol are added as cosurfactant, the microemulsion regions are considerably enlarged (Košak et al., 2004).

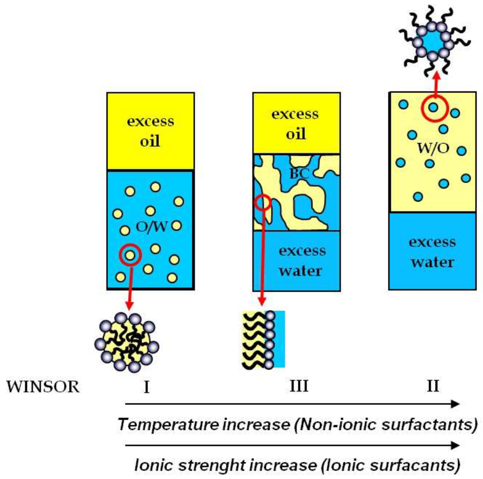


Fig. 2. Winsor classification of microemulsion equilibria. Microemulsion phase sequence as a function of temperature and salinity for non-ionic and ionic surfactants, respectively.

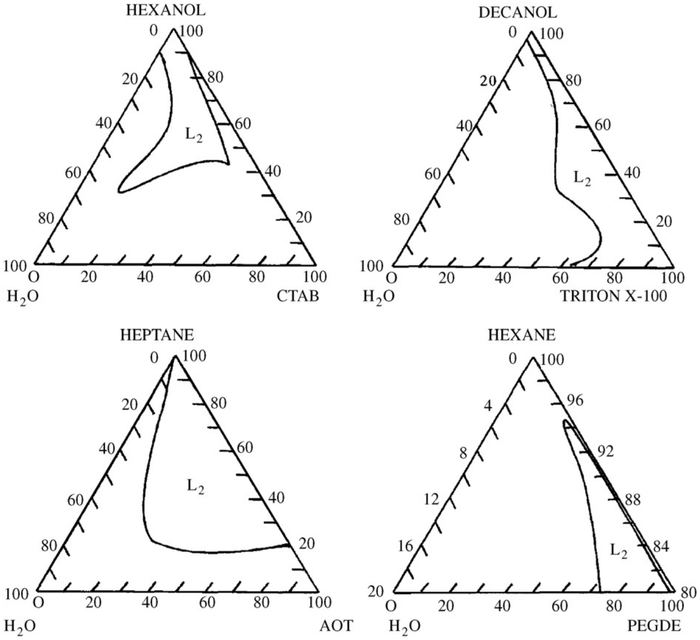


Fig. 3. Water / Nonionic surfactant / Oil pseudo bynary phase diagram, as a function of temperature. Reproduced with permission (Destrée & Nagy, 2006).

As for non-ionic surfactant – based systems, Triton® X-100 (octyl-phenol ethoxylate) is one of the most used, however, alkyl-phenol ethoxylate surfactants such as this one have a limited biodegradability. Their metabolites of degradation have low solubility and are toxic, for example, nonylphenol has been proven to be an endocrine disrupter (Jobling & Sumpter, 1993). On the other hand, aliphatic fatty alcohol ethoxylates such as PEGDE (penta(ethylene glycol) dodecyl ether) are more environmentally friendly; for nanoparticle synthesis, the technical-grade options are usually chosen due to their lower cost. A special feature of non-ionic surfactant systems is the sensitivity of their hydrophilic-lipophilic properties to temperature, and although sometimes this characteristic is seen as a drawback, the possibility for phase-behavior tuning can be used as an advantage for the formulation of non-ionic microemulsions. In addition, nonionic surfactants have a great capacity of hydration by their ethoxylated (EO) units; hence, an appropriate selection of surfactant, oil and precursor salts/precipitating agent concentration, in combination with the rich structural behavior that such a system may display as a function of temperature, can lead to highly optimized formulations in terms of aqueous phase uptake and hence reactants loading. A good premise to this behavior is the enormous efficiency boost in the formation of middle phase microemulsions by the use of block copolymer surfactants reported by Strey et al. (Jakobs et al., 1999).

2.3 Effect of precursor salts and additives on the phase behavior

Although nonionic microemulsion systems are mainly affected by temperature changes, the addition of electrolytes and cosurfactant can also produce shifts in the solubilization and

T_{HLB} (hydrophilic-lipophilic balanced temperature or phase inversion temperature) of the systems (Aramaki et al., 2001; Kunieda et al., 1995; Shinoda, 1968). The use of ionic surfactants may have some drawbacks, as usually the aqueous phase uptake of ionic microemulsions is reduced in the presence of precursor salts due to screening effects, and hence microemulsion regions become smaller (Liu et al., 2000; Gianakas et al., 2006). Additionally, complex species could interfere with particle growth by adsorption to their surface, and contaminations of ceramic nanoparticles with the surfactant counterions aer possible. Often, the effect of addition of precursor salts or precipitating agent on the phase behavior and structure of microemulsion systems is underlooked. Generally two microemulsions with a fixed water/surfactant ratio are prepared without taking into account the influence the added salt has on the size and the structure of the water droplets.

Recently, Stubenrauch et al (Magno et al., 2009) and Sanchez-Dominguez et al. (Aubery et al., 2011) have reported systematic studies on the effects of addition of reactants to nonionic microemulsion systems. It was shown (Magno et al., 2009) that, depending on the aqueous nature of nonionic microemulsion systems, and the salting-in or salting-out effect of the additives, both increase or decrease on the water solubilization could be obtained. The same group studied the effects of different salts on the water solubilization of ionic microemulsions of the system aqueous phase / AOT/butanol /decane (Stubenrauch et al., 2008). They found that depending on the type of precursor (salts of Pt, Bi, or Pb) or the reducing agent ($NaBH_4$), different behaviors can be obtained, and it was necessary to add different amounts of SDS and 1-butanol in order to keep both the w/o nature of the microemulsion droplets as well as their size (which was only assessed theoretically based on microemulsion composition).

In the studies by our group on the effects of addition of precursor salts and precipitating agent to the non-ionic microemulsion system aqueous solution / Synperonic® 13/6.5 / isooctane (Aubery et al., 2011), several factors were taken into account: phase behavior (pseudoternary phase diagrams at constant temperature), dynamicity (presence or absence of percolation in W/O structures, or formation of bicontinuous microemulsions), and droplet size (DLS). It was possible to obtain w/o microemulsions at a wide range of overlapping compositions for both precursor salts and precipitating agent. In fact, the microemulsion regions were considerably enlarged upon addition of precursors and precipitating agent; this behavior is contrary to what is typically obtained with ionic systems which have their microemulsion region reduced with addition of salts. It was difficult to obtain both type of microemulsions in either a non-percolated or percolated state; this was characterized extensively by conductivity, FT PGSE NMR and hydrophilic dye diffusion studies. When pseudobinary phase diagrams as a function of temperature were carried out, there were some compositions and temperatures at which both precursor salts and precipitating agent microemulsions were either percolated, not percolated or bicontinuous.

2.4 Dynamic processes

Among the dynamic processes in microemulsions, interactions of droplets components and droplet- droplet interactions must be taken into account (Fletcher et al, 1987; Fletcher & Horsup, 1992; Moulik & Paul, 1998). Concerning interactions of droplets components in a W/O nonionic microemulsion, a schematic representation is depicted in Figure 4. The example concerns an aqueous droplet stabilized by a mixture of surfactant and cosurfactant molecules. The aqueous domain is composed by bounded water (hydrating the surfactant/cosurfactant hydrophilic domains) and free water (forming the droplet core). The exchange process to reach microemulsion equilibria comprises: 1) exchange of water between the bounded and free state; 2) exchange of cosurfactants among the interfacial film, the continuous phase and the dispersed phase (depending on its solubility). If ionic species are solubilized in the aqueous solution, they exchange ions between the bounded and free water. The composition of the aqueous droplets, their concentration and the temperature are mayor factors defining further interactions between them.

Droplet-droplet interactions depend strongly on droplet concentration, solvent viscosity, temperature, rigidity or flexibility of interfacial layer, and interactions between surfactant tails (Capek, 2004; Lopez-Quintela, 2003). When water or oil droplet dispersions are present, the droplets continuously collide, break apart, aggregate and break apart giving rise to dynamic processes in microemulsions. These dynamic processes allows microemulsion droplets to continuously exchange their content in microsecond scales. The composition of the aqueous droplets, as explained above, has a great influence on droplet interactions. As an example, the interfacial layer plays an important role on the formation, stability and discrete nature of microemulsion droplets. The film rigidity has been observed to increase with the surfactant hydrocarbon chain, whereas it substantially decreases with cosurfactant addition. The surfactant packing capacity can be also affected by the ionic strength of the droplets (Aramaki et al., 2001; Kunieda et al., 1995). The increase of surfactant molecules in the layer is proportional to the rigidity of the micelles.

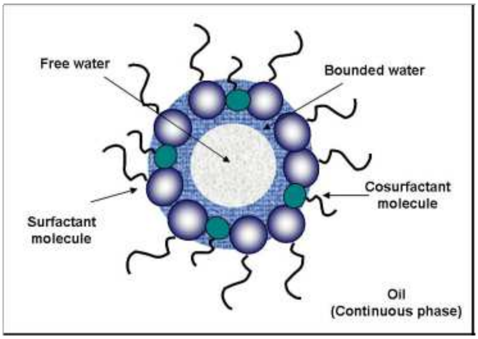


Fig. 4. Schematic representation of W/O microemulsion droplet. (Adapted with permission from Moulik, 1998).

Changes on microemulsion dynamics giving rise to structural transitions can be explained in terms of percolation. Figure 5 refers to a percolation process taking place in W/O microemulsions (Borkovec et al., 1988), as the oil to water ratio ϕ_o is varied. As observed in Figure 5, at high oil concentration, the fraction of water in discrete droplets increases with water composition (decreasing oil concentration) up to a concentration, where it drastically decreases. This concentration is called Percolation Concentration C_P. Although clusterization occurs below C_P (low water concentrations), these clusters remain finite in size respect to the bulk solution. C_P represents the concentration at which the first infinite cluster appears. Further increase on water concentration would lead to the disappearance of discrete water droplets to give rise to an increase of infinite water and oily domains, which are characteristic of bicontinuous microemulsions. Water percolation can also be induced by temperature, and is defined as the percolation temperature T_P.

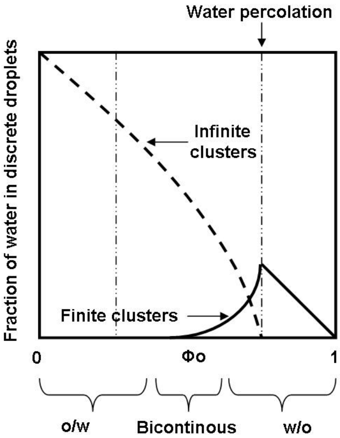


Fig. 5. Schematic representation of structural regimes of microemulsions caused by water percolation as a function of the relative amount of oil. Reprinted (adapted) with permission from Borkovec M., Eicke H.-F., Hammerich H., & Das Gupta, B. (1988) *J. Phys. Chem.,* 92, 1, pp. (206-211). Copyrigh (1988) American Chemical Society

3. The microemulsion reaction method: introduction and generalities

A brief description of the synthesis of nanoparticles in W/O microemulsions has already been given in Section 1, along with an explanatory figure (Figure 1). Colloidal nanoparticle formation is a complex process, which includes nucleation and growth steps -giving rise to nanoparticle formation- as well as eventual coagulation and flocculation.

3.1 Mechanism of nanoparticle formation

A model of particle precipitation in a homogeneous aqueous medium has been proposed by La Mer (La Mer & Dinegar, 1950). The model involves particle nucleation at short times. As soon as monomer formation takes place due to chemical reaction, its concentration increases up to the point of spontaneous nucleation, which occurs over a critical supersaturation concentration $[C]_C$. Afterwards, growth takes place (Figure 6). The growing step is mainly controlled by the diffusion of monomers in solution (C) onto the particles surface. Thus, C reaches a maximum and afterwards it begins to decrease. This decrease in monomer concentration is due to the growth of the particles by diffusion. In microemulsions, the number of nucleated sites is expected to be higher, comparing to homogeneous reactions, as illustrated in Figure 6. On the other hand, the diffusion controlled particle growth should occur at lower rate. Another model is based on the thermodynamic stabilization of the particles. In this model the particles are thermodynamically stabilized by the surfactant. The size of the particles remains constant when the precursor concentration and the size of the aqueous droplets vary. Nucleation occurs continuously during the nanoparticle formation.

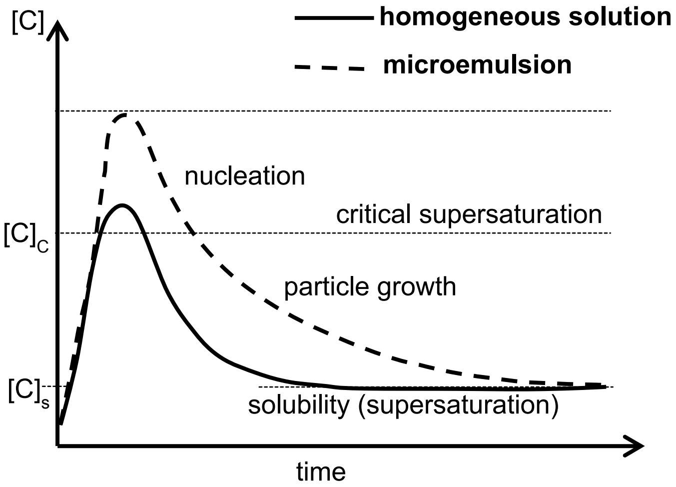


Fig. 6. Monomer concentration [C] as a function of time in microemulsions, compared to a homogeneous system. (Adapted from La Mer & Dinegar, 1950 and Schmidt, 1999).

3.2 Reaction kinetics

Although microemulsions as reaction media for the synthesis of inorganic nanoparticles have been extensively studied, the kinetics of these reactions is still not completely understood. As mentioned above, several types of nanoparticles have been synthesized using a variety of surfactant systems, and relationships between the nanoparticles characteristics and the microemulsion media are not straightforward due to the diversity of variables which can have an influence, and this may be closely related with complex kinetics. An effort to relate the surfactant media with the reaction kinetics was reviewed by Lopez-Quintela et al. (Lopez-Quintela et al., 2004), concerning both inorganic and organic syntheses in microemulsions. Few studies can be cited concerning the follow-up of reactions with time, due to the fast rate of microemulsion reactions. Some of these works are pointed out below:

1. Bandyopadhyaya et al. (Bandyopadhyaya et al., 1997) have modelized $CaCO_3$ formation in microemulsions by carbonation. A time-scale analysis was developed, resulting in a model of reaction kinetic that closely corresponded to results obtained experimentally.
2. Chew et al. (Chew et al., 1990) have studied the effect of alkanes in the formation of AgBr particles in ionic W/O microemulsions (using AOT as surfactant), where the transmittance of the reactions were followed with time with UV-Vis and Stopped-Flow Spectrophotometry. They have found an increase on reaction rate with the chain lenght of the alkane.
3. Curri et al. (Curri et al., 2000) studied the role of cosurfactant on the synthesis of CdS nanoclusters, using CTAB as surfactant. Stopped-Flow Spectrophotometry was used in order to compare a reaction using CTAB plus cosurfactant and other carried out using AOT. They have summarized two different cosurfactant effects: the influence of the

surfactant film flexibility on particle growth and the particles stabilization in solution, determined by the adsorption of cosurfactant onto the particle surface.

4. Lopez-Quintela et al. (De Dios et al., 2009) simulated the kinetics of nanoparticles formation in microemulsions. Simulations were carried out by comparing Ag, Ag-Au and Au formation with experimental data reported by Destrée and Nagy. (Destrée & Nagy, 2006). The detailed comprehension of the kinetics taking place in microemulsion reactions is limited by the experimental data in this direction. Hence, systematic studies focused on reaction rates are greatly encouraged in order to advance in this field.

3.3 Parameters influencing on nanoparticle synthesis

Although complete control of particle characteristics is still far from clear and direct, some results on this field can be pointed out as shown below.

Aqueous solution concentration. It have been described in several publications the particle size dependency with water:surfactant molar ratio (w_0). In general, it has been observed that, as increasing w_0, an increase on particle size is observed (Pileni, 1997; Lopez-Quintela, 2003). However, Cason et al. (Cason et al., 2001) have found that, with different w_0, it was possible to obtain constant particle size if the reaction time increases for the synthesis to get completed. They proposed that the growth of the particles is affected by w_0. It was considered that for low w_0 values, the aqueous solution is not enough to completely hydrate the polar groups of the surfactant and the counterion. As a consequence, the film rigidity is higher compared to higher w_0 values. This influences on the micellar exchange and, as a consequence, the growth rate decreases. Increasing w_0, the micelle rigidity decreases generating an increase in the growth rate up to a certain concentration, where further increase in w_0 simply causes reagent dilution, which causes a decrease in the growth rate. Some studies have indicated a decrease on particle size with w_0 (Bagwe & Khilar, 1997).

Reagent concentration: Particle size have been determined to be directly dependent on reagent concentration (Lopez-Quintela, 2003). An example is the work carried out by Destrée & Nagy (Destrée & Nagy, 2006). They have synthesized Pt nanoparticles, using different concentrations of K_2PtCl_4. An increase on particle diameter from 2 to 12 nm was obtained, by increasing the concentration of the precursor. On the other hand, an increase on the precipitating/precursor ratio generally causes a decrease on particle size (Lisiecki & Pileni, 2003). It is thought that increasing precipitating agent concentration, particle nucleation can be favored in a higher extent, which further grow simultaneously, resulting in particles with lower size and polydispersity.

Surfactant and cosurfactant: Studies in order to determine the effect of nonionic hydrophilic and lypophilic surfactant groups have been developed. As the lypophilic chain of the surfactant is longer, smaller particles are obtained due to the increased micellar rigidity Generally, the addition of cosurfactant causes an increase micellar exchange, due to the decrease in the interfacial film rigidity. It is thought that the increase in microemulsion droplet size is counteracted with the increase on surfactant film curvature, generating smaller particles than without cosurfactant (Lopez-Quintela et al., 2004).

Solvent: Some studies have shown that low weight oil molecules, with low molecular volumes, can penetrate in the sufactant hydrocarbon chains, increasing the film curvature and rigidity (Cason et al., 2001). This effect has been observed to produce micellar exchange decrease and, consequently, smaller particles are obtained.

Electrolytes: Some studies reveal the possible dependence of nanoparticle shape with electrolyte addition (Filankembo et al., 2003). Pileni (Pileni, 2003) has postulated that the selective ion or molecule adsorption over nanocrystal layers can affect their growth in certain directions, which could explain the apparent preference on certain particle shape.

Microemulsion structure: Some studies have claimed about the nanoparticle shape partial dependence on microemulsion structure, where the microemulsion media acts as a template. A particular example is the work carried out by Pileni (Pileni, 2001) on the preparation of Copper nanoparticles from microemulsions by varying the internal structure. Spherical water droplets resulted in spherical particles, water cilinders resulted in cylindrical copper nanocrystals (with spherical particles) and a mixture of W/O microemulsion with lamellar phase resulted in a mixture of particle shape such as spheres, cylinders, etc. It was found that the template was not the only parameter which controls the shape of nanocrystals. There are examples of nonexistent correlation between the microemulsion structure and the nanoparticles obtained, which supports the nanoparticle shape dependence on electrolyte adsorption (Chen & Lin, 2001).

Even though there is a diversity of studies carried out in order to relate nanoparticle characteristics with microemulsion properties, there is a gap in the effects of microemulsion dynamic behavior on nanoparticle characteristics, as systematic studies in this direction are scarce. The transport and micellar dynamics influence to some extent the nanoparticle formation, and it is important to take this into account in order to understand the basics of nanoparticles synthesis by this route. This type of studies may give rise to improvements on controlled nanoparticle characteristics.

4. Recent advances in the use of microemulsions as confined reaction media for the synthesis of inorganic nanoparticles

There have been a number of advances in different aspects of the synthesis of nanoparticles in microemulsions over the last four years. The main ones are: the use of other types of microemulsions for synthesis (O/W and bicontinuous microemulsions), the preparation of more complex architectures (core/shell and multishell, hybrid nanocrystals), the synthesis of more complex ceramics (spinels, perovskites, etc), modeling of reactions in microemulsions, and novel approaches for the separation of nanoparticles from the reaction mixtures. The most outstanding examples of each of these aspects are given below.

4.1 The use of other types of microemulsions for inorganic nanoparticle synthesis

One of the main drawbacks of the technique reviewed so far (synthesis in W/O microemulsions) and the main reason why it has not been generally accepted for production at the industrial scale, is the fact that these microemulsions employ large quantities of organic solvent, as well as its limited production capacity, since this is restricted to the amount of aqueous phase solubilized and the concentration of precursor which often cannot be that high due to interactions with the surfactant, as discussed in Section 2.3. Some research groups have been working in new approaches to overcome these drawbacks.

4.1.1 Synthesis in oil-in-water microemulsions

Our research group in collaboration with the group of Boutonnet, has developed a novel and straightforward approach based on O/W microemulsions (Sanchez-Dominguez et al., 2009). From a practical and environmental point of view, the possibility of preparing inorganic nanoparticles using O/W instead of W/O microemulsions may be highly advantageous, since the major (continuous) phase is water. The method consists in the use of organometallic precursors, dissolved in nanometer scale oil droplets of O/W microemulsions (Figure 7), and stabilized by a monolayer of hydrophilic surfactant. The first work reported as a proof of concept the synthesis of metallic (Pt, Pd, and Rh) as well as metal oxide (CeO_2) nanoparticles (Sanchez-Dominguez et al., 2009). Small (around 3 nm), nanocrystalline materials with a narrow size distribution were obtained (Figure 8).

It was followed by the synthesis of the following mesoporous nanocrystalline oxides: CeO_2, ZrO_2, $Ce_{0.5}Zr_{0.5}O_2$, and TiO_2 (Sanchez-Dominguez et al., 2010). Small particle size (3 nm), and high specific surface area (200-380 m^2 g^{-1}) was obtained for all materials. Nanocrystalline cubic CeO_2 and $Ce_{0.5}Zr_{0.5}O_2$ were obtained under soft conditions (35°C). The materials were evaluated as catalyst supports in the CO oxidation reaction by doping them with Au (2 wt%, impregnation technique). The resulting catalysts showed a high Au dispersion (HRTEM/EDX). These materials showed a good activity in CO oxidation at low temperature (T_{50} of 44°C for TiO_2). This study demonstrates the feasibility of this approach for the preparation of highly active catalysts.

In a more recent study by the same group (Tiseanu et al., 2011), Eu-doped luminescent CeO_2 nanocrystals were prepared by the same method. Several characterization techniques (X-ray diffraction, RAMAN spectroscopy, UV-Vis diffuse-reflectance, FTIR as well as time-resolved photoluminescence spectroscopy) were used to characterize the nanocrystals, and it was shown that there was a surface enrichment of Eu^{3+}, which diffused progressively to the inner Ceria sites upon calcination. Under excitation into the UV and visible spectral range, the calcined europium doped ceria nanocrystals display a variable emission spanning the orange-red wavelengths. A remarkable result was that the surface area of the powders remained as high as 120 m^2 g^{-1} even after calcination at 1000°C.

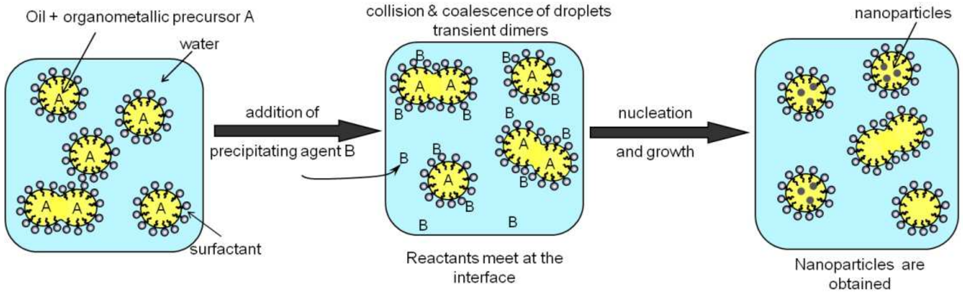


Fig. 7. TEM micrographs and related particle size distribution histograms of nanoparticles prepared in O/W microemulsions: (a) Pt, (b) Pd, (c) Rh and (d) CeO_2. Scale bar: 50 nm, except d (10 nm) and inset of d (5 nm). Reproduced with permission (Sanchez-Dominguez et al., 2009).

It should be pointed out that in all of these examples, only one microemulsion is used for synthesis, as opposed to what is typically needed with the W/O method (two microemulsions, one bearing the precursors and another one the precipitating agent in the aqueous phase). Since most precipitating agents are water-soluble, it means that it can be added directly to the microemulsion without affecting its O/W structure, and hence only one microemulsion, containing the organometallic precursor is prepared. Hence, the mechanism occurring in this approach is most likely different; possibly, it is an interfacial reaction. Modelization studies in conjunction with kinetic experiments need to be carried out in order to clarify this point. Considering these results, the perspectives of this novel O/W microemulsion reaction approach are very positive, and should complement the W/O microemulsion method, offering a greener alternative. Finally, it must be highlighted that the typical metal loading in the microemulsions reported, and hence the typical production capacity ranges from 2 to 5 grams of nanoparticles per kg of microemulsion, which is comparable and in some cases superior to typical metal loadings achieved in W/O microemulsions.

4.1.2 Synthesis in bicontinuous microemulsions

An interesting approach to boost the metal loading and hence the nanoparticle production capacity of microemulsions is the use of bicontinuous microemulsions. Lopez et al. (Esquivel et al., 2007; Loo et al., 2008) have reported this approach for the synthesis of magnetic nanoparticles. A microemulsion system based on cationic surfactants was used for the synthesis of a mixture of maghemite/magnetite nanoparticles, using bicontinuous microemulsions at 80°C, with 30-40 wt% of aqueous phase. They obtained small nanoparticles (8 nm) with a narrow size distribution, a nanocrystalline structure and superparamagnetic behavior. Furthermore, the yield of the reactions was as high as 1.16 g of product per 100 grams of microemulsion, which is rather high compared to what can be obtained in most w/o microemulsion systems (0.05 - 0.2 grams per 100 g microemulsion).

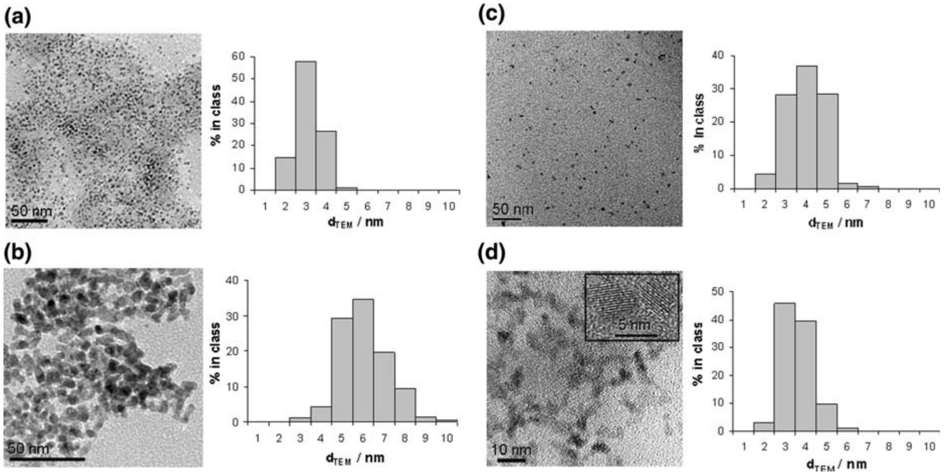


Fig. 8. TEM micrographs and related particle size distribution histograms of nanoparticles prepared in O/W microemulsions: (a) Pt, (b) Pd, (c) Rh and (d) CeO_2. Scale bar: 50 nm, except d (10 nm) and inset of d (5 nm). Reproduced with permission (Sanchez-Dominguez et al., 2009).

The same research group reported recently the synthesis of silver nanoparticles by the same approach (Reyes et al., 2010; Sosa et al., 2010), by using a microemulsion system based on AOT/SDS as the surfactant system and toluene as the oil. Depending on the surfactant: oil ratio, the authors found the formation of only globular nanoparticles or a mixture of interconnected, worm-like structures plus globular nanoparticles. The reaction yields for these materials was also remarkably high (up to 1.4 g of silver nanoparticles per 100 g of microemulsion). In all of these works, only one microemulsion was necessary for nanoparticle preparation, as the precipitating agent was added directly, as an aqueous solution, to the microemulsion containing the metallic precursors. This aspect also contributes to the greener quality of this approach as compared to the traditional W/O microemulsion reaction method.

4.1.3 Synthesis in microemulsions with an optimized aqueous phase uptake

In the work carried out by our group concerning a nonionic system (Aubery et al., 2011), large microemulsion regions were obtained when the reactants were incorporated, as mentioned in Section 2.3. Thanks to this high aqueous phase uptake and the overlap of microemulsion regions for both precursor salts and precipitating agent, synthesis of Mn-Zn ferrite nanoparticles could be carried out using a wide range of compositions. Futhermore, different scenarios were available for nanoparticle synthesis: W/O non-percolated, W/O percolated, and bicontinuous microemulsions. Differences were observed in the characteristics of the synthesized nanoparticles depending on the type of microemulsions used, and in all cases spinel nanocrystalline particles with superparamagnetic properties were obtained, directly in the microemulsion, without the need for calcination. The aqueous phase content ranged from 5 wt% to 50 wt%, which represents a boost in the production capacity. This study should encourage further research into optimized non-ionic microemulsion systems, since although the presence of salts affects their phase behavior, it does so in such a way that aqueous solubilization can be significantly increased at a certain temperature, which can be investigated by phase behavior studies.

4.2 Preparation of more complex architectures

In this regard, most of the studies concern core-shell studies, although some other structures include multiple core-shell particles, hollow spheres and nanowires and nanorods.

4.2.1 Core/shell nanoparticles

A large majority of the core-shell nanoparticles synthesized in W/O microemulsions contain silica, usually as the shell material. In the last few years, the W/O microemulsion approach has been gaining popularity over the well-known adaptation of the Stöber method (Nann & Mulvaney, 2004), for coating a diversity of nanoparticles with a silica shell. This is because it has been observed that the microemulsion method results in a better shell thickness control (Dong H, 2009), as compared to the adapted Stöber method, which is based on the sol-gel technique. It must be pointed out that in the majority of the studies, the core material was synthesized in a previous step, by a different method, usually hydrothermal or solvothermal techniques (Dong B. et al., 2009; Dong H et al., 2009; Qian et al., 2009; Vogt et al., 2010; Wang J. et al., 2010). Nevertheless, a very interesting point from these investigations is the strategy on how this silica shell is deposited onto the core; this sophisticated approach is probably the reason for the high control achieved. The core nanoparticles are usually functionalized for one or two purposes: one is in order to be very well dispersed in one of the microemulsion phases (the oily or the aqueous phase), the other is for very controlled deposition of silica via hydrolytic copolymerization with silanized molecules such as (3-aminopropyl)triethoxysilane (APTES), which were covalently linked to the core particles. By this approach, uniform CdTe@silica nanoparticles with a regular core – shell structure, 48±3 nm in diameter were obtained by Dong H. et al. (Dong H. et al., 2009). In their work, the initial core CdTe particles, synthesized by a hydrothermal method, were functionalized with thioglycolic acid, so they could be reacted with APTES and then dispersed in the aqueous phase of the microemulsion. The silica precursor, TEOS, was dissolved in the oily phase of the microemulsion (cyclohexane and octanol), and the silica shell was then formed by addition of ammonia. In the work by Dong B. et al (Dong B. et al., 2009), on the other hand, the core ZnS:Mn particles were functionalized with oleic acid and hence dispersed in the oil phase of the microemulsion, and the silica layer was deposited by reacting TEOS with ammonia in the W/O microemulsion containing the core particles dispersed in the oil. Figure 9 shows TEM results of these core-shell particles.

Fewer examples deal with the formation of core-shell nanoparticles in which both the core and the shell have been synthesized in a W/O microemulsion (Chung et al., 2011; Takenaka et al., 2007). Takenaka et al. prepared Ni nanoparticles in a W/O microemulsion, and afterwards TEOS and ammonia were added in order to form the silica layer. Core-shell nanoparticles with 20-50 nm diameter and a Ni shell (5 nm) were formed. For comparison, silica nanoparticles were prepared also in W/O microemulsions but the Ni nanoparticles were prepared by impregnation of these silica nanoparticles. Their catalytic activity in the partial oxidation of methane reaction was evaluated, and the core-shell nanoparticles had a better performance than the impregnated ones (Takenaka et al., 2007). On the other hand, Chung et al. prepared silica nanoparticles coated with a thin layer of CeO_2, and the material was also prepared in W/O microemulsions in a two-step procedure (Chung et al., 2011). This reaction turned out to be challenging as the formation of CeO_2 shell was competing with bulk precipitation. The problem was overcome by coupling two strategies:

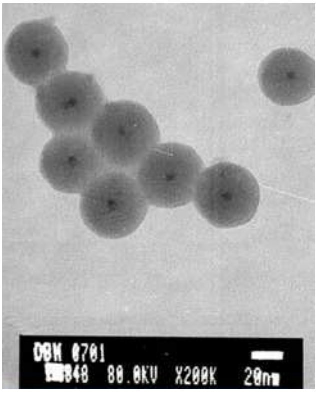


Fig. 9. TEM image of ZnS:Mn@silica nanoparticles with a core – shell structure.
(Reproduced with permission, Dong B. et al. 2009).

functionalization of the surface of the core silica nanoparticles with an organoamine group, and step-wise, semi-batch addition of the second microemulsion containing the Ce precursor. In this way, the silica cores were homogenously coated with a CeO_2 shell.

As for core-shell nanoparticles made up of materials different from silica, the synthesis of both the core and the shell is usually carried out in W/O microemulsions, either in a two step process by preparing first the core and the later deposition of the shell (by adding more aqueous phase or more microemulsion comprising the second component), or both precursors are incorporated simultaneously, but the different reaction kinetics for each of the products results in a core-shell structure. The following core-shell nanomaterials can be listed: $Pt@CeO_2$ (Yeung & Tsang, 2009 and 2010), Co@Ag (Garcia-Torres et al., 2010), $Fe_2O_3@Au$ (Iglesias-Silva et al., 2010), Ni@Au (Chiu et al., 2009), Ag@Polystyrene (Li et al., 2009), and $CdS@TiO_2$ (Ghows & Entezari, 2011). So far, the core@shell structures of these materials is not as well defined and controlled as that obtained with core@silica materials.

4.2.2 Hollow nanospheres

Jiang et al. have prepared hollow nanospheres of Ni (Jiang et al., 2010) and CuS (Jiang, 2011), by following an approach which resembles that reported by Sanchez-Dominguez et al. (Sanchez-Dominguez et al., 2009). Jiang et al. used an o/w microemulsion in which the precursor (a naphtenate), was dissolved in the oil phase (dimethylbenzene) of a water/SDS/butanol/dimethylbenzene microemulsion. The precipitating agent was added in the water phase. The authors explain that an interfacial reaction occurs, and hollow nanospheres of about 100-200 nm are formed (Figure 10, for Ni hollow spheres). These are made-up of smaller nanoparticles. One difference between Jiang's method and that reported by Sanchez-Dominguez et al is that in the former, the temperatures used for reaction are higher (85°C for Ni; post-synthesis hydrothermal treatment for CuS), whereas in the latter the temperatures used are near room temperature (25-35°C).

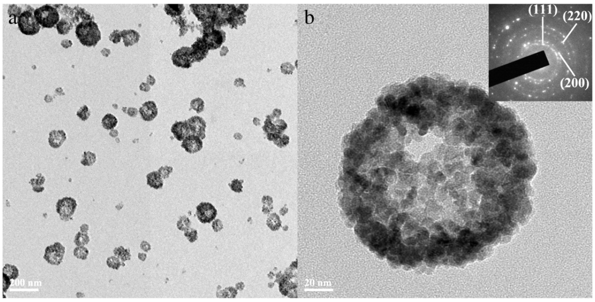


Fig. 10. TEM image of the Ni hollow spheres and (b) a single Ni hollow sphere. Inset: SAED pattern. Reproduced with permission (Jiang et al., 2010).

4.2.3 Nanowires, nanorods

Some works describe the formation of nanowire-like or nanorod structures. Usually, in order to obtain such high aspect ratio structures, it is necessary to carry out the synthesis at a relatively high temperature, or include a certain post-synthesis thermal treatment. Wang et al. synthesized single-crystalline ZnO nanowire bundles with a length of about 1 μm and a diameter of about 20–30 nm (Wang G. et al., 2010). The approach was by reacting zinc acetate with hydrazine in a w/o microemulsion based on water/dodecylbenzene sulfonic acid sodium salt /xylene. The reaction temperature is not mentioned, however for reflux of xylene is achieved around 140°C. The relatively high reaction temperature and the heating time is possibly the driving force for the growth of the nanowires, as different structures were obtained at shorter reaction times. Also, it must be pointed out that the precursor used, zinc acetate, is soluble in both water and the oil phase, which is an unusual approach.

Wu et al. synthesized nanowires of Zn/Co/Fe layered double hydroxides using a w/o microemulsion based on water/CTAB/n-hexanol n-hexane (Wu et al., 2010). In their approach, the sulfate salts were used as precursors, hence these were dissolved in the aqueous phase only, and urea was used as precipitant. The influence of reaction temperature, time, urea concentration and CTAB to water molar ratio on the structure and morphology of Zn/Co/Fe-layered double hydroxides was investigated. The possible reason for nanowire growth is the solvothermal treatment of the reaction mixture which was carried out in an autoclave at 80-180°C during 6-24 hours. The thermal treatment in the autoclave was a key factor for annealing and therefore obtaining both a crystalline structure and formation of high aspect ratio particles (nanowires).

4.3 Synthesis of complex ceramics

The w/o microemulsion reaction method has been used for the synthesis of complex ceramic nanoparticles such as perovskites, spinels, aluminates, and hexaferrites. Often, nanoparticles of precursors such as hydroxides or other amorphous compounds are synthesized in the microemulsions, and these are afterwards calcined at a certain temperature in order to obtain the desired crystalline structure.

He et al. synthesized nanoparticles of perovskite-type oxides $La_{0.8}Ce_{0.2}Cu_{0.4}Mn_{0.6}O_3$ and $La_{0.8}Ce_{0.2}Ag_{0.4}Mn_{0.6}O_3$ (He et al., 2007). The microemulsion used was CTAB/butanol /water /heptane, and for comparison purposes, the same materials were synthesized by the sol-gel technique. The precipitation of the precursors was carried out with NaOH for the microemulsion method, whereas citric acid was used for the sol-gel method. The particle size distribution was smaller and more uniform and the specific surface area was higher for the particles synthesized in microemulsions than those synthesized by sol-gel. Furthermore, the catalytic activity in the NO reduction by CO was evaluated. Performance of perovskites synthesized in microemulsion was superior than that of materials synthesized by sol-gel.

Gianakas et al. (Gianakas et al., 2007) reported the synthesis of spinel-type metal aluminates MAl_2O_4 sutwhere M=Mg, Co, o Zn using w/o and bicontinuous microemulsions. They carried out a very complete phase behavior study, which included pseudoternary phase diagrams for each precursor combination as well as the precipitating agent, ammonia. The microemulsion system was: aqueous solution/ CTAB/butanol/ octane. The spinel structure was achieved after calcination at 800°C. It was found that spinels synthesized in reverse microemulsions showed better surface and textural properties, as well as smaller particle size than spinel synthesized in bicontinuous microemulsions. As for catalytic activity, which was evaluated in the NO reduction by CO, the spinels synthesized in w/o microemulsions was slightly superior. Similar characteristic size was obtained by Wang et al. (Wang Y. et al.,

2007) for nanoparticles of manganese-doped barium aluminate $BaAl_{12}O_{19}$: Mn^{2+}; calcination at 1300°C was carried out in order to obtain the crystalline phase expected. The evaluation of photoluminescent properties of this material showed that this phosphor is a good candidate to replace Hg lamps.

Other good examples of ceramic materials obtained in w/o microemulsions include: barium hexaferrite ($BaFe_{12}O_{19}$) nanoparticles (Xu et al., 2007), tungsten oxide (WO_3) nanoparticles (Asim et al., 2007), and rutile TiO_2 nanoparticles (Keswani et al., 2010). In the last example, it is remarkable that the rutile phase was obtained at room temperature, without the need for thermal treatment, hence the size of the rutile nanocrystals remained as small as 4 nm.

4.4 Modeling of reactions in microemulsions

There have been a number of studies dealing with the theoretical aspects of nanoparticle formation by the microemulsion reaction method. Most of these studies use the Monte Carlo method. The studies carried out in the last four years are focused on several aspects: kinetics of nanoparticle formation (de Dios et al., 2009), formation of bimetallic nanoparticles (Tojo et al., 2009; Angelescu et al., 2010), droplet exchange (Niemann & Sundmacher, 2010), cluster coalescence (Kuriyedath et al., 2010), and core-shell nanoparticle formation (Viswanadh et al., 2007).

Kinetics of nanoparticle formation in microemulsion were studied for the Ag and Au nanoparticles using Monte Carlo simulations by de Dios et al. (de Dios et al., 2009). It was shown that, although the material interdroplet exchange depends primarily on the flexibility of surfactant film, a slow reaction rate leads to a more effective material interdroplet exchange for a given microemulsion. Two factors contribute to this result. Firstly, a slow reaction implies that autocatalytic growth takes place for a longer period of time, because there are available reactants. If the reaction is faster, the reactants are almost exhausted at early stages of the process. As a consequence, autocatalytic growth is only possible at the beginning. Secondly, a slow reaction rate implies the continuous production of seed nuclei, which can be exchanged between micelles due to their small size, allowing the coagulation of two nanoparticles. This exchange only takes place at early stages of the synthesis. Both factors, autocatalysis and ripening, favor the slow growth of the biggest nanoparticles leading to the production of larger particles when the reaction is slower.

With respect to the formation of bimetallic nanoparticles in microemulsions, the same research group (Tojo et al., 2009), carried out Monte Carlo studies in order to explain the different structures that can be obtained when bimetallic nanoparticles are synthesized in microemulsions. They observed that the difference in reduction rates of both metals is not the only parameter to determine metal segregation; the interdroplet channel size also plays an important role. The reduction rate difference determines nanoparticle structure only in two extreme cases: when both reactions take place at the same rate, a nanoalloy structure is always obtained. In contrast, if both reactions have very different rates, the nanoparticle shows a core-shell structure. However, in the large interval between both extreme cases, the nanoparticle structure is strongly dependent on the intermicellar exchange, which is mainly determined by the flexibility of the surfactant film around the microemulsion droplets. In a related study by Angelescu et al. (Angelescu et al., 2010), it was found that the bimetallic nanoparticle structure is mainly determined by the difference in the reduction rates of the two metal ions and the excess of reducing agent. An intermetallic structure is always obtained when both reduction reactions take place at about the same rate. When the metal ions have very different reduction potentials, a core-shell to intermetallic structure transition is found at increasing the excess of the reducing agent. An enhancement of the intermetallic structure at the expense of the core-shell, can be obtained either by decreasing the concentration of both metal salts or by increasing the interdroplet exchange rates. The results obtained by these studies has positive implications in the general formation of bimetallic nanoparticles with a given structure (core-shell or nano-alloy).

4.5 Novel approaches for the separation of nanoparticles from reaction mixtures

Often, the nanoparticles formed in a microemulsion are so well dispersed in the reaction media that some solvent has to be added in order to destabilize the microemulsion, which causes desorption of surfactant from the particles, which aggregate and precipitate, making their separation by centrifugation or filtration easier. Sometimes, during this aggressive process the nanoparticles end up so agglomerated that it is difficult to re-disperse them. Some novel and straightforward approaches have been proposed for an improved recovery or phase transfer of nanoparticles from microemulsion media.

Eastoe et al. (Hollamby & Eastoe, 2009; Myakonkaya et al., 2010, 2011; Nazar et al., 2011; Vesperinas et al., 2007) have proposed three approaches for nanoparticle recovery. One of them is based on the use of a photodestructible surfactant for microemulsion formation, and in the final step, irradiation with UV-light induces microemulsion destabilization and hence separation of Au nanoparticles (Vesperinas et al., 2007). In another approach, excess water is added at the end of the reaction, to the microemulsion containing the nanoparticles, inducing a change in phase behavior and hence microemulsion destabilization, followed by phase separation. Interestingly, by this approach, usually the nanoparticles remain in the oil phase, which can be diluted with organic solvents to form stable nanoparticle dispersions (Nazar et al., 2011). This method shows potential benefits for dispersion, storage, application, and recovery of NPs, with the great advantage that it is not necessary to add organic solvents for nanoparticle separation. In other approach by the same group, nanoparticle separation has been achieved by changing the solvent quality, for example, adding squalene to water/AOT/octane microemulsion containing Au nanoparticles (Myakonkaya et al., 2010).

Abecassis et al. have proposed nanoparticle separation by thermally inducing the phase separation of the microemulsion media (Abecassis et al., 2009). This was applied to the synthesis of Au NPs, which upon destabilization remained preferentially in the oil phase.

5. Conclusions and perspectives

It has been shown that the microemulsion reaction method is a versatile technique, useful for the controlled synthesis of a large variety of nanomaterials, from metals, metal oxides, ceramics, quantum dots, magnetic nanoparticles, etc. The method has now been extended to the synthesis of other types or architectures, such as core-shell, multishell, hollow spheres and nanowires, in addition to the traditional small globular particles. Although for about 25 years only w/o microemulsions were used for the synthesis of inorganic nanoparticles, in the last five years the use of o/w and bicontinuous microemulsions has also been developed, and their usefulness for the synthesis of a variety of nanomaterials has been demonstrated. These developments are greener than the traditional w/o microemulsion method, so it should contribute to an advance towards the industrial use of microemulsions for nanoparticle synthesis. Furthermore, there have been efforts towards boosting the metal loading in microemulsions, in order to increase their production capacity. The investigations on novel approaches for nanoparticle recovery should also be taken into account by more research groups for the improvement of nanoparticle quality and dispersability in different media. The new developments reviewed here should encourage the preparation of novel materials with different architectures, in order to respond quickly to the demands of Nanotechnology and Materials Science. It is hoped that this chapter is useful to students and researchers who start exploring the microemulsion reaction method for nanoparticle synthesis, as well as for those not new to the field but who are looking for the newest trends in this fascinating technique.

6. Acknowledgements

The authors acknowledge financial support by Ministerio Ciencia e Innovación (MICINN Spain, grant number CTQ2008-01979) and Generalitat de Catalunya (Agaur, grant number 2009SGR-961).

7. References

Abecassis B., Testard F., & Zemb T. (2009) Gold nanoparticle synthesis in worm-like catanionic micelles: Microstructure conservation and temperature induced recovery. *Soft Matter*, 5, 5, (March 2009), pp. (974-978).

Angelescu D. G., Magno L. M., & Stubenrauch C. (2010) Monte Carlo simulation of the size and composition of bimetallic nanoparticles synthesized in water in oil microemulsions. *J. Phys. Chem. C*, 114, 50, (Dec. 2010), pp. (22069-22078).

Aramaki K., Hayashi T., Katsuragi T., Ishitobi M., & Kunieda H. (2001) Effect of Adding an Amphiphilic Solubilization Improver, Sucrose Distearate, on the Solubilization Capacity of Nonionic Microemulsions, *J. Colloid Interface Sci.*, 236, 1, (April 2001), pp. (14-19).

Asim N., Radiman S., & bin Yarmo M. A. (2007) Synthesis of WO3 in nanoscale with the usage of sucrose ester microemulsion and CTAB micelle solution. *Mater. Lett.*, 61, 13, (May 2007), pp. (2652-2657).

Aubery C., Solans C., & Sanchez-Dominguez, M. (2011) Tuning high aqueous phase uptake in nonionic w/o microemulsions for the synthesis of Mn-Zn ferrite nanoparticles: phase behavior, characterization and nanoparticle synthesis. *Langmuir*, 27, 23, (Oct. 2011), pp. (14005–14013).

Bagwe R. P., & Khilar K. C. (1997) Effects of the Intermicellar Exchange Rate and Cations on the Size of Silver Chloride Nanoparticles Formed in Reverse Micelles of AOT. *Langmuir*, 13, 24, (Nov. 1997), pp. (6432-6438).

Bandyopadhyaya R., Kumar R., Gandhi K. S., & Ramkrishna, D. (1997) Modeling of Precipitation in Reverse Micellar Systems, *Langmuir*, 13, 14, (July 1997), pp. (3610-3620).

Borkovec M., Eicke H.-F., Hammerich H., & Das Gupta, B. (1988) Two Percolation Processes in Microemulsions. *J. Phys. Chem.*, 92, 1, (Jan 1988), pp. (206-211).

Boutonnet M., Kizzling J., & Stenius P. (1982) The preparation of monodisperse colloidal metal particles from microemulsions. *Colloids and Surfaces*, 5, 3, (November 1982), pp. (209-225)

Boutonnet M., Lögdberg S., & Svensson E. E. (2008) Recent developments in the application of nanoparticles prepared from w/o microemulsions in heterogeneous catalysis. *Curr. Opin. Colloid Interface Sci*., 13, 4, (August 2008), pp. (270-286).

Capek, I. (2004) Preparation of metal nanoparticles in water-in-oil (wyo) microemulsions. *Adv. Colloid Interface Sci.* 2004, 110, 1-2, (June 2004), pp. (49-74)

Cason J. P., Miller M. E., Thompson J. B., & Roberts C. B. (2001) Solvent Effects on Copper Nanoparticle Growth Behavior in AOT Reverse Micelle Systems. *J. Phys. Chem. B.*, 105, 12, (March 2001), pp. (2297-2302).

Chen C. C., & Lin J. J. (2001) Controlled Growth of Cubic Cadmium Sulfide Nanoparticles Using Patterned Self-Assembled Monolayers as a Template. *Adv. Mater.*, 13, 2, (Jan, 2001), pp. (136-139).

Chew C. H., Can L. M., & Shah D. O. (1990) The Effect of Alkanes On The Formation Of Ultrafine Silver Bromide Particles In Ionic W/O Microemulsions. *J. Dispersion Sci. Technol.*, 11, 6, (Dec. 1990), pp. (593-609).

Chiu H. K., Chiang I. C., & Chen D. H. (2009) Synthesis of NiAu alloy and core-shell nanoparticles in water-in-oil microemulsions. *J. Nanopart. Res.*, 11, 5, (July 2009), pp. (1137-1144).

Chung S. H., Lee D. W., Kim M. S., & Lee K. Y. (2011) The synthesis of silica and silica-ceria, core-shell nanoparticles in a water-in-oil (W/O) microemulsion composed of heptane and water with the binary surfactants AOT and NP-5. J. Colloid Interface Sci., 355, 1, (March 2011), pp. (70-75).

Clarke S., Fletcher P. D. I., & Ye X. (1990) Langmuir, 6, 7, (July 1990), pp. (1301-1309).

Cross, J. (1987). Nonionic Surfactants: Chemical Analysis, Surfactant Science Series (1st edition), Marcel Decker Inc., ISBN-10: 0824776267, New York, NY, USA.

Curri M. L., Agostiano A., Manna L., Della Monica M., Catalano, M., Chiavarone L., Spagnolo V., & Lugara M. (2000) Synthesis and Characterization of CdS Nanoclusters in a Quaternary Microemulsion: the Role of the Cosurfactant *J. Phys. Chem. B*, 104, 35, (August 2000), pp. (8391-8397).

Cushing B. L., Kolesnichenko V. L., & O'Connor C. J. (2004) Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles. *Chem. Rev.*, 104, 9, (Nov. 2004), pp. (3893-3946).

Danielsson I., and Lindman B. (1981) The definition of microemulsion. *Colloids and Surf*aces, *3*, 4, (December 1981) pp. (391-392).

De Dios M., Barroso F., Tojo C., & Lopez-Quintela, M. A. (2009) Simulation of the kinetics of nanoparticle formation in microemulsions. *J Colloid Interface Sci.*, 333, 2, (May 2009), pp. (741-748).

Destrée C., & Nagy J. B. (2006) Mechanism of formation of inorganic and organic nanoparticles from microemulsions. *Adv. Colloid Interface Sci.*, 123-126, (November 2006), pp. (353-367).

Dong B., Cao L., Su G., Liu W., Qu H., & Jiang D. (2009) Synthesis and characterization of the water-soluble silica-coated ZnS:Mn nanoparticles as fluorescent sensor for Cu^{2+} ions. *J. Colloid Interface Sci.*, 339, 1, (Nov. 2009), pp. (78-82).

Dong H., Liu Y., Ye Z., Zhang W., Wang G., Liu Z., & Yuan J. (2009) Luminescent nanoparticles of silica-encapsulated cadmium-tellurium (CdTe) quantum dots with a core-shell structure: Preparation and characterization. Helvetica Chimica Acta, 92, 11, (Nov. 2009), pp.(2249-2256).

Eastoe J., Hollamby M. J., & Hudson L. (2006) Recent advances in nanoparticle synthesis with reversed micelles, *Adv. Colloid Interface Sci.*, 128-130, (December 2006), pp. (5-15).

Esquivel J., Facundo I. A., Treviño M. E., & López R. G. (2007) A novel method to prepare magnetic nanoparticles: precipitation in bicontinuous microemulsions. *J. Mater. Sci.*, 42, 21, (Nov. 2007), pp. (9015–9020)

Filankembo A., Giorgio S., Lisieki I., & Pileni, M. P. (2003) Is the Anion the Major Parameter in the Shape Control of Nanocrystals? *J. Phys. Chem. B*, 107, 30, (April 2003), pp. (7492-7500).

Fletcher P. D. I., Howe A. M., & Robinson B. H. (1987) J. Chem. Soc. Faraday Trans. 1, The kinetics of solubilisate exchange between water droplets of a water-in-oil microemulsion, 83, 4, (April 1987), pp. (985-1006).

Fletcher P. D. I., & Horsup D. I. (1992) Droplet dynamics in water-in-oil microemulsions and macroemulsions stabilised by non-ionic surfactants. Correlation of measured rates with monolayer bending elasticity. *J. Chem. Soc. Faraday Trans. 1*, 88, 6, (June 1992), pp. (855-864).

Gaertner, G.F., & Lydtin H. (1994) Review of ultrafine particle generation by laser ablation from solid targets in gas flows. *Nanostructured Mater.*, 4, 5, (September 1994), pp. (559-568).

Garcia-Torres J., Vallés E., & Gómez E. (2010) Synthesis and characterization of Co@Ag core-shell nanoparticles. *J. Nanopart. Res.*, 12, 6, (August 2010), pp. (2189-2199).

Gautam U. K., Ghosh M., Rajamathi M., & Seshadri R. (2002) Solvothermal routes to capped oxide and chalcogenide nanoparticles, *Pure Appl. Chem.*, 74, 9, (September 2002), pp. (1643-1649).

Ghows N., & Entezari M. H. (2011) Fast and easy synthesis of core-shell nanocrystal (CdS/TiO2) at low temperature by micro-emulsion under ultrasound. *Ultrason. Sonochem.*, 18, 2, (March 2011), pp. (629-634).

Giannakas A. E., Ladavos A. K., Armatas G. S., Petrakis D. E., & Pomonis P. (2006) Effect of composition on the conductivity of CTAB butanol octane nitrate salts ($Al(NO_3)_3$ + $Zn(NO_3)_2$) microemulsions and on the surface and textural properties of resulting spinels $ZnAl_2O_4$. *J. Appl. Surf. Sci.*, 252, 6, (Jan. 2006), pp. (2159-2170).

Giannakas A. E., Ladavos A. K., Armatas G. S., & Pomonis P. J. (2007) Surface properties, textural features and catalytic performance for NO + CO abatement of spinels MAl_2O_4 (M = Mg, Co and Zn) developed by reverse and bicontinuous microemulsion method. *Appl. Surface Sci.*, 253, 16, (June 2007), pp. (6969-6979).

He H., Liu M., Dai H., Qiu W., & Zi X. (2007) An investigation of NO/CO reaction over perovskite-type oxide $La_{0.8}Ce_{0.2}B_{0.4}Mn_{0.6}O_3$ (B = Cu or Ag) catalysts synthesized by reverse microemulsion. *Catal. Today*, 126, 3-4, (August 2007), pp. (290-295).

Hollamby M. J., Eastoe J., Chemelli A., Glatter O., Rogers S., Heenan R. K., & Grillo, I. (2010) Separation and purification of nanoparticles in a single step. *Langmuir*, 26, 10, (May 2010), pp. (6989-69949.

Holmberg K. (2004) Surfactant-templated nanomaterials synthesis. *J. Colloid Interface Sci.*, 274, 2, (June 2004), pp. (355-364).

Iglesias-Silva E., Vilas-Vilela J. L., López-Quintela M. A., Rivas J., Rodríguez M., & León L. M. (2010) Synthesis of gold-coated iron oxide nanoparticles. *J. Non-Cryst. Solids*, 356, 25-27, (June 2010), pp. (1233-1235).

Jakobs B., Sottman T., Strey R., Allgaier J., Willner L., & Richter D. (1999) Amphiphilic Block Copolymers as Efficiency Boosters for Microemulsions, *Langmuir*, 15, 20, (Sep. 1999), pp. (6707-6711).

Jiang D., Deng Y., Wang H., Shen B., Wu Y., Liu L., Zhong C., & Hu W. (2010) Fabrication of Nickel hollow spheres by microemulsion-template-interface reaction route. *Mater. Lett.* 64, 6, (March 2010), pp. (746-7489).

Jiang D., Hu W., Wang H., Shen B., & Deng Y. (2011) Microemulsion template synthesis of copper sulfide hollow spheres at room temperature. *Colloids Surface A: Physicochem. Eng. Aspects*, 384, 1-3, (July 2011), pp. (228-232).

Jobling S., & Sumpter J. P. (1993) Detergent components in sewage effluent are weakly oestrogenic to fish: An in vitro study using rainbow trout (Oncorhynchus mykiss) hepatocytes. *Aquatic Toxicology*. 27, 3-4, (Dec. 1993), pp. (361-372).

Keswani R. K., Ghodke H., Sarkar D., Khilar K. C., & Srinivasa, R. S. (2010) Room temperature synthesis of titanium dioxide nanoparticles of different phases in water in oil microemulsion. *Colloids Surface A: Physicochem. Eng. Aspects*, 369, 1-3, (Oct. 2010), pp. (75-81).

Košak A., Makovec D., & Drofenik M. (2004) The preparation of MnZn-ferrite nanoparticles in a water/CTAB, 1-butanol/1-hexanol reverse microemulsion, *Phys. Stat. Sol. C*, 1, 12, (Dec. 2004), pp. (3521-3524)

Kruis F. E., Fissan H., & Peled A. (1998) Synthesis of nanoparticles in the gas phase for electronic, optical and magnetic applications—a review. *J. Aerosol Sci.* 29, 5-6, (June 1998), pp. (511-535).

Kunieda H., & Friberg S.E. (1981) Critical Phenomena in a Surfactant/Water/Oil System. Basic Study on the Correlation between Solubilization, Microemulsion, and Ultralow Interfacial Tensions. *Bull. Chem. Soc. Jpn*, 54, 4, (April, 1981), pp (1010-1014).

Kunieda, H.; Nakano, A.; Pes, M. A. (1995) Effect of Oil on the Solubilization in Microemulsion Systems Including Nonionic Surfactant Mixtures, *Langmuir*, 11, 9, (Sep. 1995), pp. (3302-3306).

Kuriyedath S. R., Kostova B., Kevrekidis I. G., & Mountziaris T. J. (2010) Lattice Monte Carlo simulation of cluster coalescence kinetics with application to template-assisted synthesis of quantum dots. *Ind. Eng. Chem. Res.* 49, 21, (Nov. 2010), pp. (10442-104499.

La Mer V., & Dinegar R. (1950) Theory, Production and Mechanism of Monodisperse Hydrosols. *J. Am.Chem. Soc.*, 72, 11, (Nov. 1950), pp. (4847-4854).

Li Y. C., Wang C. P., Hu P. F., & Liu, X. J. (2009) A method for synthesizing the core (Ag)/shell (PSt) composite nanoparticles. *Mater. Lett.*, 63, 20, (August 2009), pp. (1659-1661).

Lindman B., & Friberg S. E.(1999) Chapter 1: Microemulsions: A Historical Overview, In: *Handbook of Microemulsion Science and Technology*, Eds. Kumar, P.; Mittal, K.L., pp. (1-12), Marcel Dekker, Inc., ISBN: 0-8247-1979-4, New York, NY, USA.

Lisiecki I., & Pileni M. P. (2003) Synthesis of Well-Defined and Low Size Distribution Cobalt Nanocrystals: The Limited Influence of Reverse Micelles, *Langmuir*, 19, 22, (Sep. 2003), pp. (9486-9489).

Liu C., Rondinone A. J., & Zhang Z. J. (2000) Synthesis of magnetic spinel ferrite $CoFe_2O_4$ anoparticles from ferric salt and characterization of the size-dependent superparamagnetic properties. *Pure Appl. Chem.*, 72, 1-2, (Jan. 2000), pp. (37-45).

Loo A. L., Pineda M. G., Saade H., Treviño M. E., & Lopez, R.G. (2008) Synthesis of magnetic nanoparticles in bicontinuous microemulsions. Effect of surfactant concentration. *J. Mater. Sci.*, 43, 10, (May 2008), pp. (3649–3654).

López-Quintela M. A. (2003) Synthesis of nanomaterials in microemulsions: formation mechanisms and growth control. *Curr. Opin. Colloid Interface Sci.*, 8, 2 (June 2003), pp. (137-144).

López-Quintela M. A., Tojo C., Blanco M. C., García Rio L., & Leis J. R. (2004) Microemulsion dynamics and reactions in microemulsions. *Curr. Opin. Colloid Interface Sci.*, 9, 3-4 (November 2004), pp. (264-278).

Magno M., Angelescu D. G, & Stubenrauch, C. (2009) Phase diagrams of non-ionic microemulsions containing reducing agents and metal salts as bases for the synthesis of bimetallic nanoparticles, *Colloids Surfaces A: Physicochem. Eng. Aspects*, 348, 1-3, (Sep 2009), pp. (116-123)

Moulik S. P., & Paul B. K.(1998) Structure, dynamics and transport properties of microemulsions, *Adv. Colloid Interface Sci.*, 78, 2, (Sep. 1998), pp. (99-195).

Myakonkaya O., Deniau B., Eastoe J., Rogers S. E., Ghigo A., Hollamby M., Vesperinas A., Sankar M., Taylor S. H., Bartley J. K., & Hutchings G. J. (2010) Recycling nanocatalysts by tuning solvent quality. *J. Colloid Interface Sci.*, 350, 2, (Oct. 2010), pp (443-446).

Myakonkaya O., Eastoe J., Mutch K. J., & Grillo I. (2011) Polymer-induced recovery of nanoparticles from microemulsions. *Phys. Chem. Chem. Phys.*, 13, 8, (Sep. 2010), pp. (3059-3063).

Nann T., & Mulvaney P. (2004) Single Quantum Dots in Spherical Silica Particles. *Angew. Chem. Int. Ed.*, 43, 40, (Oct. 2004), pp. (5393–5396).

Nazar M. F., Myakonkaya O., Shah, S. S., & Eastoe J. (2011) Separating nanoparticles from microemulsions. *J. Colloid Interface Sci.*, 354, 2, (Feb. 2011), pp. (624-629).

Niemann B., & Sundmacher K. (2010) Nanoparticle precipitation in microemulsions: Population balance model and identification of bivariate droplet exchange kernel. *J. Colloid Interface Sci.*, 342, 2, (Feb. 2010), pp. (361-371).

Pileni M. P., Zemb T., & Petit C. (1985) Solubilization by reverse micelles: Solute localization and structure perturbation. *Chem. Phys. Lett.* 118, 4, (August 1985), pp(414–420).

Pileni M. P. (1997) Nanosized Particles Made in Colloidal Assemblies. *Langmuir*, 13, 13, (June 1997), pp. (3266-3276).

Pileni M.P. (1998) Fabrication and Properties of Nanosized Material Made by Using Colloidal Assemblies as Templates, *Cryst. Res. Technol.*, 33, 7-8 (Dec. 1998), pp. (1155-1186)

Pileni M. P. (2001) Mesostructured Fluids in Oil-Rich Regions: Structural and Templating Approaches, *Langmuir*, 17, 24, (Nov. 2001), pp. (7476-7486).

Pileni M. P. (2003) The role of soft colloidal templates in controlling the size and shape of inorganic nanocrystals. *Nat. Mater.*, 2, 3 (March 2003), pp. (145-150).

Qian L. P., Yuan D., Yi G. S., & Chow G. M. (2009) Critical shell thickness and emission enhancement of $NaYF_4$:Yb,Er/$NaYF_4$/silica core/shell/shell nanoparticles. J. Mater. Res., 24, 12, (Jan 2009), pp. (3559-3568).

Qiao, S. Z., Liu J., & Lu G. Q. M. (2011) Chapter 21: Synthetic Chemistry of Nanomaterials, In: *Modern Inorganic Synthetic Chemistry*, Eds. Xu, R.; Pang, W.; Huo, Q., pp. (479-506) Elsevier, ISBN 13: 978-0-444-53599-3, Amsterdam, The Netherlands.

Reyes P. Y., Espinoza J. A., Treviño M. E., Saade H., & López R. G. (2010) Synthesis of Silver Nanoparticles by Precipitation in Bicontinuous Microemulsions. *J. Nanomaterials*, Volume 2010, Article ID 948941, 7 pages. doi:10.1155/2010/948941

Sanchez-Dominguez M., Boutonnet M., & Solans C. (2009) A novel approach to metal and metal oxide nanoparticle synthesis: the oil-in-water microemulsion reaction method. *J. Nanopart. Res.*, 11, 7, (Oct. 2009), pp. 1823-1829

Sanchez-Dominguez M., Liotta L. F., Di Carlo G., Pantaleo G., Venezia A. M., Solans C., & Boutonnet M. (2010) Synthesis of CeO_2, ZrO_2, $Ce_{0.5}Zr_{0.5}O_2$, and TiO_2 nanoparticles by a novel oil-in-water microemulsion reaction method and their use as catalyst support for CO oxidation. *Catal. Today*, 158, 1-2, (Dec. 2010), pp. (35-43)

Schmidt J., Guesdon C., & Schomäcker R. (1999). Engineering aspects of preparation of nanocrystalline particles in microemulsions. *J. Nanopart.Res.,* 1, 2, (June 1999), pp.(267-276).

Shinoda K. (1968) Proceedings of 5th Int. Congr. Detergency, Barcelona, Spain, September 1968, p. 275.

Sosa Y. D., Rabelero M., Treviño M. E., Saade H., & López R. G. (2010) High-Yield Synthesis of Silver Nanoparticles by Precipitation in a High-Aqueous Phase Content Reverse Microemulsion, *J. Nanomaterials*, Volume 2010, Article ID 392572, 6 pages doi:10.1155/2010/392572

Stubenrauch C., Wielpütz T., Sottmann T., Roychowdhury C., & Di Salvo F. J. (2008) Microemulsions as templates for the synthesis of metallic nanoparticles. *Colloids Surfaces A: Physicochem. Eng. Aspects*, 317, 1-3, (March 2008), pp. (328–338)

Suslick K. S., Hyeon T., & Fang M. (1996) Nanostructured Materials Generated by High-Intensity Ultrasound: Sonochemical Synthesis and Catalytic Studies. *Chem. Mater.* 8, 8, (August 1996), pp. (2172-2179).

Takenaka S., Umebayashi H., Tanabe E., Matsune H., & Kishida, M. (2007) Specific performance of silica-coated Ni catalysts for the partial oxidation of methane to synthesis gas. J. Catal. 245, 2, (Jan. 2007), pp. (392-400).

Tiseanu C., Parvulescu V. I., Boutonnet M., Cojocaru B., Primus P. A., Teodorescu C. M., Solans C., & Sanchez-Dominguez M. (2011) Surface versus volume effects in luminescent ceria nanocrystals synthesized by an oil-in-water microemulsion method. Phys. Chem. Chem. Phys., 13, 38, (August 2011), pp. (17135–17145)

Tojo C., De Dios M., & López-Quintela M. A. (2009) On the structure of bimetallic nanoparticles synthesized in microemulsions. *J. Phys. Chem. C*, 113, 44, (Nov. 2009), pp. (19145-19154).

Vesperinas A., Eastoe J., Jackson S., & Wyatt P. (2007) Light-induced flocculation of gold nanoparticles. *Chem. Commun.*, 43, 38, (August 2007), pp. (3912-3914).

Viswanadh B., Tikku S., & Khilar K. C. (2007) Modeling core-shell nanoparticle formation using three reactive microemulsions. *Colloids Surfaces A: Physicochem. Eng. Aspects*, 298, 3, (May 2007), pp. (149-157).

Vogt C., Toprak M. S., Muhammed M., Laurent S., Bridot J. L., & Müller R. N. (2010) High quality and tunable silica shell–magnetic core nanoparticles, *J. Nanopart. Res.,* 12, 4, (May 2010), pp. (1137-1147).

Wang G., Deng Y., & Guo L. (2010) Single-crystalline ZnO nanowire bundles: Synthesis, mechanism and their application in dielectric composites. *Chem. Eur. J.*, 16, 33, (Sep. 2010), pp. (10220-10225).

Wang, J., Tsuzuki T., Sun L., & Wang X. (2010) Reverse microemulsion-mediated synthesis of SiO_2-coated ZnO composite nanoparticles: Multiple cores with tunable shell thickness. *ACS Appl. Mater. Interfaces*, 2, 4, (March 2010), pp. (957-960).

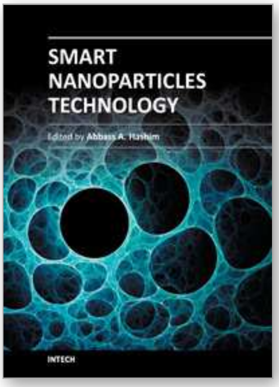
Wang Y. H., & Li F. (2007) Synthesis of $BaAl_{12}O_{19}:Mn^{2+}$ nanophosphors by a reverse microemulsion method and its photoluminescence properties under VUV excitation. *J. Lumin.*, 122-123, (Jan-April 2007), pp. (866-868).

Wu H., Jiao Q., Zhao Y., Huang S., Li X., Liu H., & Zhou M. (2010) Synthesis of Zn/Co/Fe-layered double hydroxide nanowires with controllable morphology in a water-in-oil microemulsion. *Mater. Charact.*, 61, 2, (Feb. 2010), pp. (227-232).

Yeung C. M. Y., & Tsang S. C. (2009) Noble metal core-ceria shell catalysts for water-gas shift reaction. J. Phys. Chem. C, 113, 15, (April 2009), pp. (6074-6087).

Yeung C. M. Y., & Tsang S. C. (2010) Some optimization in preparing core-shell Pt-ceria catalysts for water gas shift reaction. *J. Mol. Catal. A: Chem.*, 322, 1-2, (May 2010), pp. (17-25).

Xu P., Han X., & Wang, M. (2007) Synthesis and magnetic properties of $BaFe_{12}O_{19}$ hexaferrite nanoparticles by a reverse microemulsion technique. *J. Phys. Chem. C,* 111, 16, (April 2007), pp. (5866-5870).



Smart Nanoparticles Technology
Edited by Dr. Abbass Hashim

ISBN 978-953-51-0500-8
Hard cover, 576 pages
Publisher InTech

How to reference

Margarita Sanchez-Dominguez, Carolina Aubery and Conxita Solans (2012). New Trends on the Synthesis of Inorganic Nanoparticles Using Microemulsions as Confined Reaction Media, Smart Nanoparticles Technology, Dr. Abbass Hashim (Ed.), ISBN: 978-953-51-0500-8, InTech, Available from: http://www.intechopen.com/books/smart-nanoparticles-technology/new-trends-on-the-synthesis-of-inorganic-nanoparticles-using-microemulsions-as-confined-reaction-med

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821