Synthesis of nanomaterials in microemulsions: formation mechanisms and growth control

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Abstract

The evolution of the microemulsion technique in the last years is revised with special emphasis in the mechanisms of control of particle size, namely the control by the proper microemulsions and the control by the surfactant adsorption (capping). The kinetics of the particle formation; the possibility of the preparation of coatings, core-shell and ‘onion-like’ structures with a very precise size control; the use of microemulsions to produce fine ceramics and finally their use in the preparation of superlattices is addressed. © 2003 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Microemulsions are colloidal ‘nano-dispersions’ of water in oil (or oil in water) stabilized by a surfactant film. These thermodynamically stable dispersions can be considered as truly nanoreactors which can be used to carry out chemical reactions and, in particular, to synthesize nanomaterials. The main idea behind this technique is that by appropriate control of the synthesis parameters one can use these nanoreactors to produce tailor-made products down to a nanoscale level with new and special properties. This is a very expanding area and we will describe here our particular opinion about the most important tendencies which are now growing in this field.

2. Microemulsion technique: theoretical/simulation results

The shape (and size) of the dispersed nanodroplets is mainly governed by the curvature free energy and is determined by the elastic constant and the curvatures of the surfactant film [1]. The elasticity of the film depends not only on the surfactant type and the thermodynamic conditions, but also on the presence of additives, like alcohols, electrolytes, block copolymers and polyelectrolytes. In the past, mainly spherical (and in some cases elongated) nanodroplets have been used to prepare nanoparticles of different kind of materials and it was assumed that the size and shape of these nanodroplets could ‘template’ the synthesis of nanomaterials [2]. However, one has to take into account the dynamic nature of the microemulsions. Due to the Brownian motion these droplets collide forming a fused dimer (or an encounter pair) and interchange reactants with a rate constant $k_{\text{ex}}$. The above described parameters, which determine the elasticity of the surfactant film, influence also the reactant interchange among the nanodroplets. The interdroplet exchange of the particles growing inside the droplets is inhibited by the inversion of the film curvature in the fused dimer which, in turns, depends on the film flexibility (Fig. 1). All of this has to be taken into account to understand the particle size control in microemulsions. Because a lot of parameters with different influences enter into consideration, in the last years Monte Carlo simulations have been performed trying to get some light into the ‘jungle’ of experimental results. In a series of papers [3–6] Tojo et al. developed further a previous Monte Carlo simulation procedure [7,8] in which the following parameters have explicitly being included: the film flexibility through a parameter $f$ proportional to $\kappa^{-3/2}$ being $\kappa$ the curvature elastic modulus; the interdroplet exchange rate constant $k_{\text{ex}}$; concentration of reactants $c$; reactant excess ratio $x$;
droplet size $R$ (which is controlled by the ratio $w = [\text{H}_2\text{O}]/[\text{surfactant}]$); volume fraction $\varphi$; and critical nucleus $n^*$. Two more aspects were considered in the simulation, namely, the possibility of autocatalysis of the reaction by the already formed sub-nanoparticles (clusters) and the possibility of ripening. Even for a Monte Carlo study this is a very time consuming task. Therefore, until now only a restricted parameter space could be explored assuming that reactions are performed by mixing two identical microemulsions carrying the reactants. It turns out that many of the previous ideas put forward to explain the experimental results, based on simulation results Tojo et al. [7] who found a bimodal distribution at high flexibilities, intermediate values of $k_{\text{ex}}$ and high concentrations. Based on simulation results Tojo et al. [7] have reinterpreted the experimental results obtained by Bagwe and Khilar [11] about the effects of $k_{\text{ex}}$ on the Ag particle size prepared in different AOT microemulsions. At this point it should be convenient to highlight some results obtained from the simulations and put together with recent experimental results:

1. **Control of particle size by reactant concentration.** The increase of particle size (and polydispersity) by increasing the concentration is predicted (bimodality is obtained for rigid films, as it was previously stated). Experimentally observed in the formation of Cu nanoparticles in SDS/ethanol $\mu$Es [12]; zirconia particles in Arlacel/IPA $\mu$Es [13]; CF$_3$ particles in T154 [14].

2. **Decrease of particle size by increasing the excess of one of the reactants until a plateau is reached at high excesses.** This has been observed in the formation of Ni [15] and Pd [16] particles in CTAB/ethanol $\mu$Es.

3. **Increase of particle size by increasing the surfactant film flexibility.** The increase in flexibility can be achieved by increasing the amount of cosurfactant (alcohols), approaching to the microemulsion instability phase boundaries, changing the droplet size, changing the chain length of the oil or cosurfactant, etc. Observed in the formation of Ni and Pd in CTAB/ethanol $\mu$Es [15,16]; tungstic acid in TX-100/ethanol $\mu$Es [17]; Cu$_2[\text{Fe(CN)}_6]$ AOT $\mu$Es [18]; CdS in CTAB/ethanol $\mu$Es [19]; Rh in CTAC/ethanol [20].

4. **Increase of particle size by increasing the droplet size.** In principle, a linear relationship should be expected, but one has to consider that, in many cases, because of the associated increase of the flexibility with droplet size these two effects are superimposed and a much larger increase of the particle size is observed, as it was found, e.g. by Panda et al. [17] and Moulik et al. [18]. This effect should be less important working with more rigid surfactant films. So, for example, good linear correlations between the particle size and the mole ratio $w$ are reported by Qiu et al. [12]; Althues and Kaskel [21] and are in agreement with other previous reports (see e.g. [22]).

It has to be pointed out that all simulations were performed under the assumption that the chemical reaction used to produce the particles is much faster than the material interchange, which is the most usual case.
In the opposite case, the most simple bulk ideas of nucleation and growth can be used to explain the experimental results using a pseudophase reaction model. This has been carried out, e.g. by Osseo-Asare and Arriagada [23] to explain the formation of silica particles in NP-5 μEs.

3. Particle stabilization: surfactant adsorption and capping

One interesting aspect which should be now considered is directly related to the particle size control by the adsorption of surfactants onto the particles. This has been observed very often in the formation of particles in μEs (see e.g. [24]). The surfactant adsorption can stop the growth of the particles inside the microemulsion droplets. The particle control by surfactant adsorption can easily be detected by the fact that the particle size is almost constant and independent of the various parameters discussed above which may affect the particle size. Because the adsorption on catalysts is favoured this size control by adsorption has been mostly found in the preparation of catalysts particles in μEs. Indeed, the paper of Boutonnet et al. [25], which is often cited as one of the first examples of preparation of particles in μEs, reveals that the particle size of Pt, Rh, Pd and Ir, in the size range 2–5 nm, is almost independent of the surfactant, water amount and reactant concentration used in the preparation. This independence of the synthesis parameters has been confirmed in recent papers [20,26*,27], although a small dependence, mainly when alcohols are used as cosurfactants, has been reported [16,20] which may be attributed to the simultaneous influence of the flexibility and differences in the surfactant adsorption. Examples of the surfactant adsorption size control have also been reported for CdS particles prepared in CTAB μEs [19**]. In all these cases the use of microemulsions to control the final size seems not to be very useful because one could obtain the same results in bulk using directly ligand or complexing stabilizing agents. Although the use of ligands to inhibit the particle growth is a well-known procedure, much older than the microemulsion technique (see e.g. [28]), the explanation of this capping control is still not clear. A statistical thermodynamic formulation was put forward by Leff et al. [29] a few years ago to explain the size control in gold nanoparticles synthesized in the presence of an alkyl thiol in a two phase aqueous/organic system. These authors predicted a minimum stable size when the surfactant is in excess and also that the particle size increases by decreasing the surfactant concentration. This can be rationalized assuming that the positive entropy change due to the adsorption of the surfactant decreases as the particle radius, R, increases (in a simple way one could think that a very small particle is like a 1D object and a large particle a 2D one, so that the entropy reduction should be larger for the adsorption onto a tiny particle, 3D→1D, than onto a bigger particle, 3D→2D). Fig. 2 schematically shows how the Gibbs energy for the formation of a surfactant capped particle would change with R. A minimum stable critical radius, $r_{\text{crit}}$, can be predicted. In the same figure, it is shown that when the microemulsion controlled radius, $r_A$, is smaller than this critical surfactant controlled radius (for example, in cases where the adsorption enthalpy is small) the final particle size is microemulsion controlled. Surfactant control occurs in the opposite case ($r_B > r_c$).

The transition from both kind of controls could explain the tendency to a plateau which has been observed in some cases for the particle size when the droplet size is increased (see e.g. [30]). It should be mentioned here that in μE control processes one can stop the growth of the nanoparticles inside the droplets by adding an appropriate capping agent (‘capping control’) to the microemulsion as has been reported by Goffredi et al. [31]. In other cases a capping agent is used to protect the particles against aggregation when they are aged or separated from the microemulsion (see e.g. [19**,32]). It should be interesting to add directly to the microemulsions a capping agent with functional properties in order to prepare functionalised particles, but we are not aware of any result in this direction and only this has been proved to work by Liao and Chen [33] through a two step process to produce yeast alcohol dehydrogenase bound to magnetic nanoparticles.

4. Kinetics of particle formation in microemulsions

No much work has been performed on this very interesting area. Turco Liveri et al. [34] studied the formation of ZnS particles in AOT μEs. Following the evolution of the wavelength at the band maximum,
which is related to the size of the particles, these authors deduced the following power law behaviour for the time evolution of particle size: \( d \alpha = l^{0.074} \). They noted that the power law exponent is much smaller than the one predicted by the Lifshitz–Slyozov law (1/3). But this is only a long-time law. At short-times a 1/6 exponent is expected [35], which still is much larger than that observed by Turco Liveri et al. However, one has to consider that the particles are growing in a restricted space for which a drastic reduction of the exponent is expected due to finite size effects as has been found by Binder and Heermann for a 3D Ising model [36]. This tells us again that the nucleation and growth processes, in these restricted geometries, are very different to the same processes observed in bulk. Differences in the kinetics depending on the used surfactant were reported by Ingelsten et al. [26*]. Explanations based on a change in the exchange rate, differences in the water droplet environments and differences in the binding possibilities are discussed. Finally, it is interesting to note that Wu et al. [37] reported the possibility that the critical nucleus, \( n^* \), may be dependent on the particle composition. In general, we feel that more experiments should be done for checking the growth laws and the kinetics in these compartmentalized media for a better understanding of the particle size control in microemulsions.

5. Coatings, core-shell and ‘onion-like’ particles

In our opinion one of the main advantages of the microemulsion method to prepare nanomaterials, over other preparation methods, is the ability to control the formation of different kind of core-shell(s) structures with sub-nanometric resolution, as it was previously demonstrated [38–40,6**]. The procedure used, schematically shown in Fig. 3, consists in a two-step process: (1) formation of uniform particles (core) with sizes smaller than the droplet sizes. According to the above mentioned ideas this can be achieved using low concentrations, excess of one of the reactants and rigid films; (2) adding new reactants for the second reaction (shell). The firstly produced particles act as nucleation centers for the second reaction. In this case autocatalysis should be favoured using stoichiometric amounts of reactants, high concentrations and rigid films [3]. The layer thickness can be controlled by the reactant concentration. Co–Ag and Fe–Cu–Fe nanoparticles with antiferromagnetic coupling between the Fe layers have been produced in this way [6**]. Based on results obtained for epitaxially grown thin films the antiferromagnetic coupling can only be possible if the intermediate non-magnetic Cu shell has an \( \approx 1 \) nm thickness with angstrom monodispersity. Although this powerful potentiality of the technique has not been fully explored, in the last years some core-shell structures have been reported: silica-coated iron oxide by Santra et al. [41*]; silica coated zinc ferrite [42*]; gold coated FePt, and CoPt, [43]. In this section one could include also some efforts which have been carried out about the encapsulation of nanoparticles with polymers either by extracting the particles from the microemulsions [44] or, more elegantly, by in situ polymerisation as it was reported for the preparation of Bi/PMMA [45], CdS/PAM nanocomposites [46*] and BaSO₄ in polymerized surfactants [10*].

6. Better ceramics through microemulsions

In the last years the formation of ceramics via microemulsion techniques has experienced a fast growth mainly because of the incorporation of the sol–gel technology into the microemulsion method (see e.g. [47]). In this way a much better control of the stoichiometry of the final product (sol–gel advantage) with a much finer and controllable grain size (microemulsion advantage) can be achieved. Examples of this interesting approach can be found in Refs. [21,48,49**,50–54]. Reports about the previous developed precipitation/coprecipitation method in microemulsions can also be found [55–59*,60,61]. The lack of methods for inhibiting the aggregation and sintering of the produced nanoparticles, when they are fired to crystallize, is a serious drawback which could be solved by the hot-fluid annealing procedure just developed by Lin et al. [62**].

7. 1D, 2D and 3D nanoparticle superlattices

This is a very fascinating area which began in the 1990s (see e.g. [28,63]) and is now emerging with enormous potentialities because of their possible and
multiple applications in the future nanotechnologies. Superlattices are made from highly monodispersed nanoparticles and are of special interest because they combine the unusual properties of the individual nanoparticles with collective effects. Although this is totally away from the scope of this article because superlattices can be made with other techniques different from the microemulsion ones (see e.g. [64]), we want to recall the attention of the reader to some recent results obtained using microemulsions by the Pilenti’s group [65**–66–68]. In all of these cases a capping agent is introduced into the microemulsions, at the end of the reaction, to achieve a better protection of the particles. However, the attained monodispersity is not enough and a selective precipitation size selection was needed to achieve the particle self-assembly. An interesting approach combining in one step the nanoparticle synthesis in microemulsions with its self-assembly has also been reported by Li et al. [69]. Vaucher et al. [70**] have also shown that 2D and 3D highly ordered square (cubic) superlattices can be obtained by a 4 days aging of a Prussian blue nanoparticle’s microemulsion. One-dimensional arrangements of nanoparticles prepared in microemulsions just by aging have also been recently reported [71,72*,73,74]. No clear reason for this anisotropic growth is known, but it seems that many parameters play an important role in the final shape and size of the observed aggregates, which are very sensitive to minor changes in the experimental conditions, as it has been observed in the formation of linear silver aggregates [75] and star-shaped cadmium [76]; but this extreme sensitivity to the experimental conditions is a fact which is already very well known in the preparation of controlled colloidal particles [77].

8. Conclusions

The microemulsion method is a very versatile technique which allows the preparation of a great variety of nanomaterials just alone or in combination with other techniques. The precise control of all the parameters which can be varied affecting the final particle sizes and shapes is still a challenge, but the richness of the possibilities which can be achieved from nano- to macro-scales is a big spur to work with these tiny dispersed droplets, where the only limitation will be our imagination. Although we have tried to cover the most important aspects related with this technique, many items have been left out for discussion, like polymerisation reactions in microemulsions [78**], synthesis of organic nanoparticles [79**], industrial uses of μEs [80,81], block copolymer μEs [82] and the use of water-in-supercritical fluid μEs [83], in particular W/CO₂ supercritical μEs [84–86], which could make this a more friendly environmental and ‘green’ technique.

Acknowledgments

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References and recommended reading

● of special interest

●● of outstanding interest


An interesting paper dealing with the possibility of cosurfactant adsorption (not absorption!) onto the CdS nanoparticles.

The possibility that pentanol behaves as capping agent at high concentrations and some differences about the kinetics depending on the used µEs are reported.


An interesting paper dealing with the possibility of cosurfactant (alcohol) adsorption (not absorption!) onto the CdS nanoparticles. The possibility that pentanol behaves as capping agent at high concentrations and some differences about the kinetics depending on the used µEs are reported.


Santra S, Tappe R, Theodoropoulon N, Dobson J, Hebard A. Synthesis and characterization of CdS nanoparticles in 50 nm polymer nanospheres is presented. Differences in particle size and aggregation using different surfactants are first studied. A 1 nm silica coating is reported which can be further functionalised to attach oligonucleotides.


The powerful use of microemulsions to prepare core-shell nanostructures is here well-demonstrated.


An appealing single-step procedure to produce ~2 nm CdS nanoparticles in 50 nm polymer nanospheres is presented.


Very interesting paper in which the effect of the microemulsion composition, water/alkoxide ratio, aging time, recovery and drying technique, and the calcination temperature on the final size, morphology and properties of barium hexaaluminate nanoparticles is studied. A very good starting point for any one interested in the microemulsion–sol–gel processing technique.


[59] Vestal CR, Zhang JZ. Synthesis of CoCrFeO\(_3\) nanoparticles using microemulsion methods and size-dependent studies of their magnetic properties. Chem Mater 2002;14:3817–22. CoCrFeO\(_3\) bulk materials prepared from nanoparticles synthesized in microemulsions show a different magnetic behaviour than the bulk material prepared by conventional ceramic route. Another example of the much higher homogeneity which can be achieved by the microemulsion route.


The very simple and extremely useful idea of using low-temperature in situ annealing to crystallize the microemulsion prepared nanoparticles is reported.


An interesting report on the fabrication of 2D and 3D self organised nanoparticle arrangements. Optical, electrical and magnetic properties of Ag, S, Ag and Co superlattices are described.


A beautiful example of how nanoparticle crystal superlattices can be made in a single-step procedure.


The formation of inorganic salt nanowires is studied showing a clear transition nanoparticles–networks–short wires–long wires as the aging time increases.


A complete revision of the state-of-the-art in this interesting field.


The influence of different experimental parameters, including the way of stirring, volume of the solution, vessel geometry, etc. on the final particle size and number of particles are studied. Some hypothesis about the particle formation mechanism are proposed.


Interesting approach to produce in a simple way nanostructured coatings.


