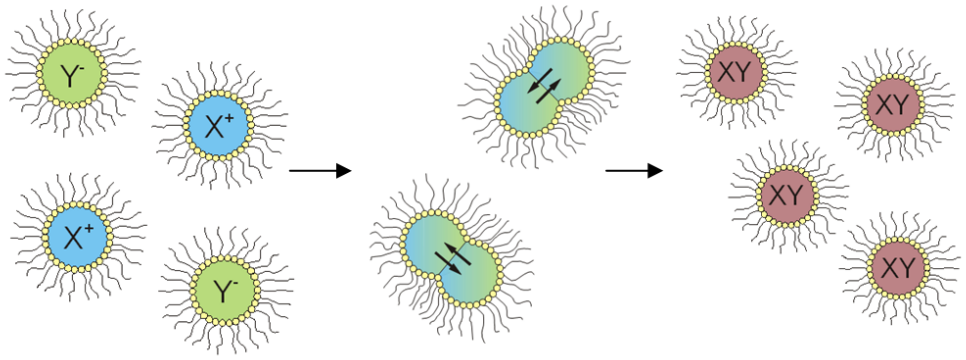
1. Literature Review: Nanoparticle Synthesis in Reversed Micelles*



Scheme 1. Simplified reaction scheme for nanoparticle synthesis in reversed micelles

1.1 Introduction

Nanoparticle synthesis in microemulsions has been a hot research topic since the early 1980s, when the first systems of platinum, palladium and rhodium metal nanoparticles were prepared.[1] Since this groundbreaking work, a huge variety of nanoparticles have been synthesized in both water-in-oil and water-in-supercritical fluid microemulsions by the process summarized in scheme 1. A database search conducted for the preparation of this article revealed 1221 references containing all keywords "nanoparticles", "synthesis" and "microemulsions" (source: Scifinder Scholar 10/11/2005), demonstrating the extent and maturity of the field. Many reviews have been written,[2-21] which arrive at different conclusions. Compiled and submitted in the 4th quarter of 2005 (and published in 2006), this review* aimed to summarize the most recent work, as well as discuss the current state of understanding about control over nanoparticle morphology and dimensions. Of special interest was the design and synthesis of nanoparticles with specific properties for advanced applications. Now up to the 1st quarter of 2009, some further developments have occurred, particularly relevant to other thesis chapters which are discussed in the penultimate section 2.5 below, “significant recent highlights”.

* Please see Eastoe, J.; Hollamby, M. J.; Hudson, L. *Adv. Colloid Interface Sci.* **2006**, *128-130*, 5-15

1.2 Water in Oil microemulsions

A microemulsion is a thermodynamically stable dispersion of two immiscible or partially miscible fluids; the system is stabilized by added surfactant(s). Different types of microemulsion are known, such as water-in-oil (w/o), oil-in-water (o/w), water-in-sc-CO_2 (w/sc-CO_2). A w/o microemulsion is formed when water is dispersed in a hydrocarbon based continuous phase, and is normally located towards the oil apex of a water/oil/surfactant triangular Gibb's phase diagram (Figure 1). In this region, thermodynamically driven surfactant self-assembly generates aggregates known as reverse or inverted micelles (e.g. L_2 phase on Figure 1),[22] of which spherical reverse micelles are the most common form. Added polar or ionic components will become compartmentalized into the central cores of these reversed micelles, hence affording fine dispersion of inorganic materials in oil. It is important to recognize that these systems are dynamic – micelles frequently collide via random Brownian motion and coalesce to form dimers, which may exchange contents then break apart again, a process which typically occurs on a time scale of 10μs-1ms.[8,23,24] Clearly, any inorganic reagents encapsulated inside the micelles will become mixed. This exchange process is fundamental to nanoparticle synthesis with reversed micellar templates, allowing different reactants solubilized in separate micellar solutions to react upon mixing. Micelles in these systems might therefore be described as "nanoreactors", providing a suitable environment for controlled nucleation and growth. In addition, at the latter stages of growth, steric stabilization provided by the surfactant layer prevents the nanoparticles from aggregating.[8]

Nanoparticles have been synthesized by this method for a variety of novel applications; topical examples include catalysts for fuel cells,[25,26] food applications,[27] nano-probes for fluorescent bioassays,[28] nano-fluids[29] and uses in de-chlorinating chlorinated olefins.[30] Other preparations have employed biocompatible microemulsions,[31] environmentally safer systems,[32,33] and use high-efficiency silicone surfactants.[34,35] More complex syntheses have also been reported, including mixed Co/Ag nanoparticles,[36] microemulsions containing monomer and initiator to form nanoparticles constrained inside a polymer matrix[37] and nanotube-containing microemulsions for generating carbon nanotube/polyaniline composites.[38] However, probably one of the most adventurous examples is the bio-mimetic "emergence" work by Mann et al.[39-45] Several extremely complex nanostructures have been produced and

superbly imaged by this group, demonstrating that this relatively straightforward method may have important applications.

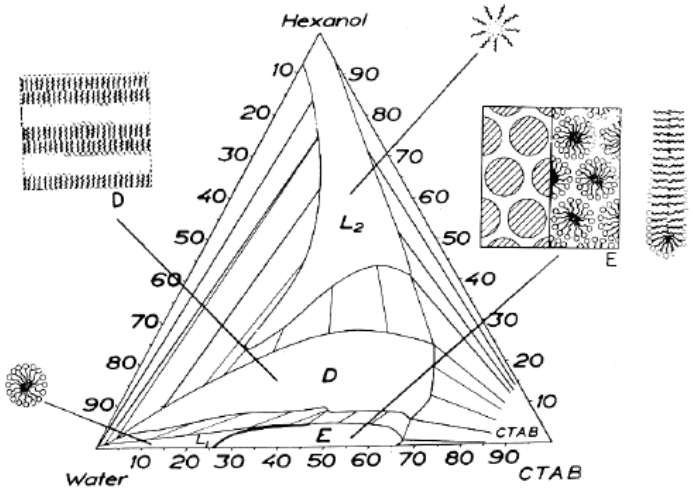


Figure 1. Phase diagram for CTAB/1-hexanol/water systems.[22]

1.2.1 Synthetic methods

A widely used approach is shown in Figure 2. This involves the preparation of two separate microemulsions, A and B, incorporating the different reactants. Upon mixing, nucleation occurs on the micelle edges as the water inside them becomes supersaturated with reactants. Growth then occurs around this nucleation point, with the arrival of more reactant fed via intermicellar exchange. A recent TEM study[46] provides insight into the process. Figure 3 shows images as the reaction proceeds; it would appear that growth initially begins at the interface, and then moves into the core of the micelle. The rate limiting step for particle growth is intermicellar exchange; microemulsion exchange characteristic times are of the order 10μs-1ms which is slow compared to diffusion of reagents inside the polar domains.[8,10] This has repercussions for reaction rates, in that the time taken for a reaction to go to completion via reversed micellar medium is vastly different from the native aqueous solution.[47] Control of this exchange, via interfacial fluidity of the surfactant membrane, is believed to be of high importance. Note that successful use of this method has also been achieved with three separate microemulsions, mixed together to produce $BaTiO_3$.[48]

Another method to synthesize nanoparticles is from a single microemulsion, a common way to produce metal nanoparticles. One of the desired reactants is solubilized inside reverse micelles, and a second reactant (typically a reductant) is added directly to the system.

Table 1 presents a compilation of several nano-materials formed using either of these methods. Despite such a large number of successes, it is not always possible to synthesize materials in this fashion. Pileni reports limitations in the approach; for example difficulties in the synthesis of either ZnTe or in incorporating Mn into either ZnTe or CdTe,[49] clearly indicating that "chemistry in colloidal self-assemblies is not always similar to that in homogeneous solutions". Recently, two novel methods have been proposed, using a single microemulsion. One involves direct reaction of silver metal solubilized in reverse micelles with the surfactant (dioctyldimethylammonium halide) counter-ion to prepare silver halides.[50,51] The other employs gamma irradiation of a micellar solution of copper nitrate to form copper metal which is then oxidized in situ to cuprous oxide.[52] In these cases, intermicellar exchange has less of an influence on the final outcome (with respect to size, polydispersity, shape), providing faster rates and new possibilities for morphological control.

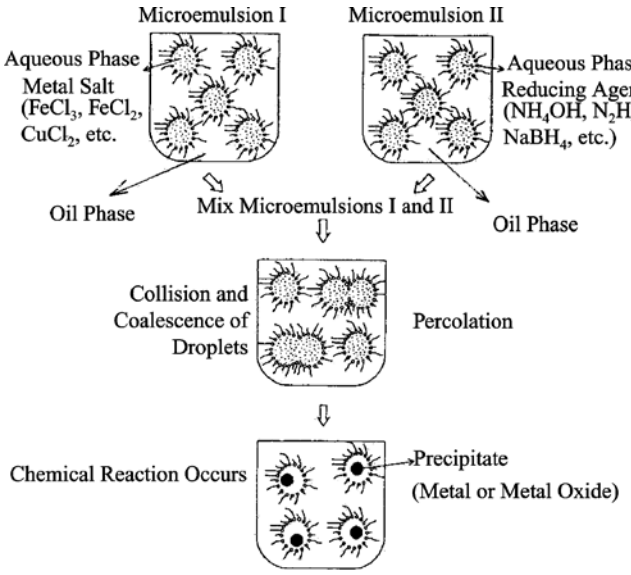


Figure 2. Proposed mechanism for the formation of nanoparticles by the microemulsion approach.[12]

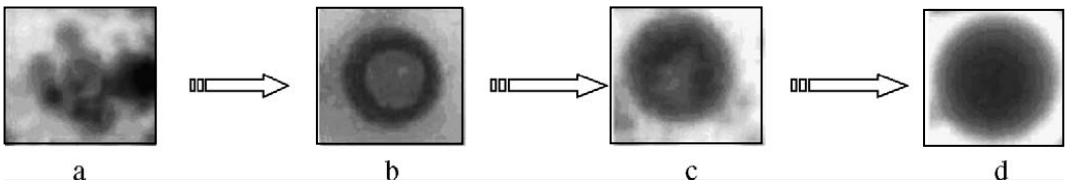


Figure 3. TEM images of ZnSe particle growth in reverse micelles.[46] Aging times: (a) 5 min; (b) 30 min; (c) 2 h; (d) 12 h after initiation of the reaction. Scale bars were not provided in the paper (ref 46) for this figure, although nanoparticle diameters were reported to be of the order 200 - 300 nm.

Metals / Alloys	Pt,[1,25] Rh,[1] Pd,[1] Cu,[7,47,53-63] Co,[64-67] Ag,[68-74] Au,[75-78] Ni[79,80]
Semiconductors	ZnS,[32,81] PbS,[82-84] CdS,[85-93] CdTe,[49] ZnSe,[46] Ce-Tb[26] and Ce-Zr[26]
Metal oxides / halides	CuO,[60,94] ZrO_2,[95] CeO_2,[96-98] TiO_2,[99 100] AgCl[50,101,102]
Other inorganic compounds	$Ca(OH)_2$,[103] $CaCO_3$,[103,104] silicate-1,[105] $Ca_3(PO_4)_2$,[33,41,106] $CaSO_4$,[107] $BaSO_4$[44,108,109]
Magnetic compounds	Fe_2O_3,[95,110] Fe_3O_4[111,112]
More complex (for applications)	$SrR_2O_4:Eu^{3+}$ where R=Y,Lu,[113] YF_3[114] $BaZrO_3/Zr_{0.95}O_2$,[115] Eu-doped Y_2O_3,[116] NiZn ferrite ($Ni_{0.5}Zn_{0.7}Fe_{1.8}O_{3.9}$),[117] $Co_3[Co(CN)_6]_2$ (analogue of Prussian blue)[118]
Polymers	polyaniline,[38,119] poly(alkylcyanoacrylate)[120]

Table 1: Nano-materials formed in w/o microemulsions

1.2.2 Particle Size Control

Five main properties of a system are thought to influence size and polydispersity: the type of solvent employed; the surfactant or co-surfactants used; addition of electrolyte; concentration of reagents; and, most controversially, the molar ratio w_0=[water]/[surfactant]. In discussing how factors affect particle size, authors frequently employ the concept of "interfacial fluidity". This term is loosely used to denote the bending elasticity/rigidity or bending modulus of the surfactant film, which

is identified in the Chemical Physics literature by well-defined quantities κ, K or "2K+KBar". Szleifer et al.[121] employed the Helfrich formula[122] to calculate the effect of different molecular factors on bending rigidities of interfacial films in microemulsions. These detailed simulations showed that:

- Bending rigidity is strongly dependent on surfactant chain length. Rigidity is predicted to increase by around an order of magnitude when chain length is doubled.
- Rigidity is decreased significantly by the addition of short-chain molecules to a longer-chain surfactant film. When half or more of the longer-chain surfactant has been replaced by shorter-chain molecules, the rigidity is shown to be essentially that of a pure short-chain film.
- A lower area-per-molecule adopted by the surfactant leads to a higher packing efficiency, and thus a more rigid film.

All of these conclusions have been backed up by rigorous experimental study.[122-124] The effect of different solvents has also been studied,[122,124] and this is found to be a second order effect when compared to the points mentioned above. The type of solvent only produces noticeable differences in rigidity for large changes in chain length.

Solvent effects

Particle size is affected by solvent type. This was shown initially by Pileni et al. in a TEM study on silver nanoparticles,[72] in which larger particles were formed in isooctane than in cyclohexane. It should be noted that a significant decrease in intermicellar exchange rate constant between the two solvents (a factor of 10) has previously been reported.[125] Bagwe and Khilar[102] and Cason et al.[47] further investigated this effect in various systems (AgCl, Cu), finding that different solvents do affect particle growth rate, final size and polydispersity. However they found that given sufficient aging time, similarly sized particles were formed in both cyclohexane and isooctane (Pileni et al. were unable to do this as their system aggregated after 1hr). Kitchens et al. conferred these results with a rigorous modeling study.[63] It could easily be imagined that by imaging the particles early on in the aging process, Pileni et al. saw an effect of solvent not on final particle size but on particle growth rate.

The change in growth rate has been explained by the authors discussed above using the argument that smaller, less bulky solvent molecules with lower molecular volumes,

such as cyclohexane, can penetrate between surfactant tails, which increases surfactant curvature and rigidity.[47] According to this theory, isooctane (being bulkier with a larger molecular volume) would not be able penetrate the surfactant tails so efficiently, thereby leading to a more fluid interface and thus faster growth rates. Although these ideas provide apparently convincing explanations of the phenomena they remain controversial. Whilst an increased rigidity at the interface might be expected to lead to a slower growth rate (given the effect on the ability for the interfacial film to split to allow dimer formation), detailed measurement has shown that solvent type has only a minor effect on surfactant film rigidities in microemulsions.[122,124] Instead, solvent molecular volume might explain the observed change in final particle size. Lopez-Quintela et al. provide a neat summary, pointing out that a more stable micelle system arises from greater interactions between the solvent and surfactant tails which in turn leads to an enhanced ability to stabilize larger particles.[8] Any increase in rate of intermicellar exchange will also result in a higher rate of growth comparable to nucleation, hence is likely to generate systems with lower polydispersity.

Note that all of the aforementioned work employed AOT (sodium di(ethyl-2-hexyl) sulfosuccinate) as surfactant. Clearly, slightly different magnitudes of solvent effect will be seen with different surfactants, but the same general principle appears to be the case. In work on copper oxide nanoparticles with the cationic CTAB (cetyltrimethylammonium bromide) and n-butanol as surfactant and co-surfactant, larger particles were generated with n-octane as solvent compared to isooctane (higher molecular volume).[94]

Surfactants and co-surfactants

The most commonly used surfactant is the anionic AOT, although a variety of common cationic surfactants are also frequently employed, such as CTAB or di-*n*-didodecyldimethylammoniumbromide (DDAB) and non-ionics Triton X100, polyoxyethylene (5) nonylphenyl ether (NP-5) or polyoxyethylene (9) nonylphenyl ether (NP-9). A more comprehensive list of the different surfactants investigated can be found in other reviews.[8,10] For some systems co-surfactants (intermediate-chain-length alcohols, such as n-butanol or n-hexanol) are also employed. With AOT, it is thought that functionalizing with a metal ion needed for the reaction, by substitution

of the sodium ion, can improve monodispersity.[4] This must be done carefully as counterion exchange can have significant effects on the stability of reversed micelles.[126] In addition, the shape of the micellar aggregates is also known to be strongly affected by the nature of the counterion.[127]

An interesting study, carried out by Lee et al.,[99] investigated the effect of surfactant structure on size of TiO_2 nanoparticles formed via hydrolysis of titanium tetraisopropoxide. Two different series of non-ionic surfactants - Brij 52,56,58 and Tween 20,60,85 were employed. For the Brij series, head group size increases from Brij 52 to Brij 58 (average number of oxyethylene groups increases from 2 to 20), but with a constant tail length (average number of hydrophobic carbons is 16). For the Tween series, head group size is essentially constant (20 oxyethylene groups) whereas the tail length varies from 20 to 48 carbons. Larger nanoparticles were favored by both smaller head groups and shorter tails. The authors theorize that smaller head groups result in less water binding to the surfactant, thereby increasing hydrolysis rates, whilst with longer tails, the "size of reverse micelles decreases because the hydrocarbon chain prohibits the access of the water near the micelles". However these conclusions are limited due to the dynamic nature of systems, and the fact that the reactions were followed for only one hour. As previously discussed, longer hydrophobic chains may lead to a more rigid interface,[121-124] thus potentially slowing intermicellar exchange and growth rate. In this case the effects of surfactant head group size on particle growth do not appear to be consistent with the film rigidity model (smaller head groups give more rigid films and therefore may be expected to yield smaller particles).

The effect of different surfactants has also been investigated by Bumajdad et al, in which nanometer sized nanocrystals of CeO_2 were synthesized with a wide range of surfactants.[98] They found the resultant nanoparticles have different shapes, sizes and stabilities. Work carried out by Spirin et al. reported that Triton X100 to be a much more suitable surfactant in the synthesis of gold nanoparticles than AOT.[75] It can therefore be concluded that whilst the choice of surfactant does influence the size, shape and stability of particles, its influence is ill-defined and poorly understood.

Both López-Quintela et al and Uskokovic have both reviewed the effect of co-surfactant on the final particle size.[8,10] In general, it was concluded that the addition of a co-surfactant leads to a higher fluidity of the interfacial film, thus increasing the rate of intermicellar exchange, but also leading to a higher curvature of the droplets, so

smaller particles. This result is in line with the work discussed above on film rigidities.[121-124] The effects of changing co-surfactant structure have recently been explored by T. Charinpanitkul et al and it appears that a decrease in particle size is observed when the co-surfactant chain length is shortened.[81]

Added Electrolyte

Work has been carried out by both Kitchens et al and Saiwan et al following the effects of added salt to the eventual particle size.[62,100] Although the initial micelle size and shape changes dramatically, it was concluded that the size of the final particles is affected only slightly by the addition of electrolyte. In addition, Kitchens et al also observed a large increase in particle growth rates with electrolyte concentration, consistent with a destabilization of the micellar system. A summary of work in this area can also be found reviewed elsewhere.[10]

Reagent concentration

Several studies have shown an increase in particle size goes hand in hand with reactant concentration.[66,67,69,111,112] The clearest example is from the work of Pileni et al,[69] who investigated the size of silver nanodisks generated as a function of the concentration of added reducing agent hydrazine. As the concentration ratio of hydrazine : AOT was increased, an increase in particle size was observed, which lead to changes in optical properties of the nanoparticle dispersion (Figure 4). A similar increase in particle size was observed by Eastoe et al. for the case of colloidal cobalt.[67] One plausible explanation is that a 'polymerization' of AOT occurs via reaction with hydrazine to form an imine dimer, which was previously shown by Clint et al.[128] Increasing reagent concentration also appears to reduce polydispersity. In studies by both Pileni et al. and Eastoe et al.,[66,83] an increase in the number of particles of a similar size were noted when concentration of reagents, $NaBH_4$ and Na_2S respectively, was raised.

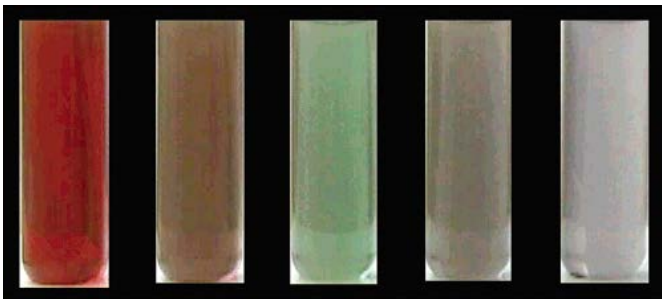


Figure 4. Dispersions of nanocrystals formed in reverse micelles and obtained at various hydrazine concentrations, y = $[N_2H_4]$ / [AOT] = 4.9, 5.8, 6.6, 8.2, and 12.3 respectively.[69]

Water content

This effect has been reviewed extensively elsewhere,[2-6,8-10,12,14] however, confusingly these papers tend to arrive at different conclusions. In most papers, water content is described by the water to surfactant molar ratio, w_0 (= $[H_2O]$/[surfactant]), however it is important to recognize that the total water in the system can be raised not only by raising w_0 but also by increasing [surfactant] at constant w_0 levels.[101] Another effect of changing w_0 is to vary the effective concentration of reagents inside the micelles, if the overall reagent concentration is kept constant. Many papers show the final particle size to be dependent on the initial w_0 demonstrating control over the outcomes of the syntheses merely by changing w_0.[2,7,34,60,80,90,93,101,103,112,114,129-132] The size of the nanocrystals produced is typically observed to differ from that of the microemulsion droplets, but this variation is strongly dependent on the nature of the chemical reaction. This observation is generally attributed to a templating effect on nanocrystal growth by the reverse micelles, following a similar relationship as the swelling law observed in water-in-oil microemulsion systems.[133,134] Unfortunately in many cases, the same effect is not seen.[8-10,14,47,63,67,83,120]

Cason et al.[47] and then Kitchens et al.[63] found that at any given value of w_0, the same size nanoparticles can be synthesized, if left for sufficient time for the reaction to go to completion (Figure 5). They proposed that the rate of nanoparticle *growth* is affected by varying w_0 (not necessarily eventual size). This can be explained as follows; at low w_0, water present inside the reverse micelles can be considered "bound", since there is insufficient available to solvate both the surfactant head group and counter ion.[2] With

the water bound, the micelle interface is said to be more "rigid", lowering intermicellar exchange and thus growth rates. As w_0 is raised, the film becomes more fluid, so the rate of growth increases, until it reaches a point when all extra water added is just added to the bulk water pool (at around w_0 = 10-15).[102,133] At this point the extra water added merely dilutes the reagents, decreasing reaction rates, so any increase in rate of intermicellar exchange from this point is negated, and in some cases a decrease in particle size is observed.[102] Whilst relatively convincing, these ideas and findings run contrary to the bulk of other work mentioned above which suggest that particle size can indeed be controlled by w_0.

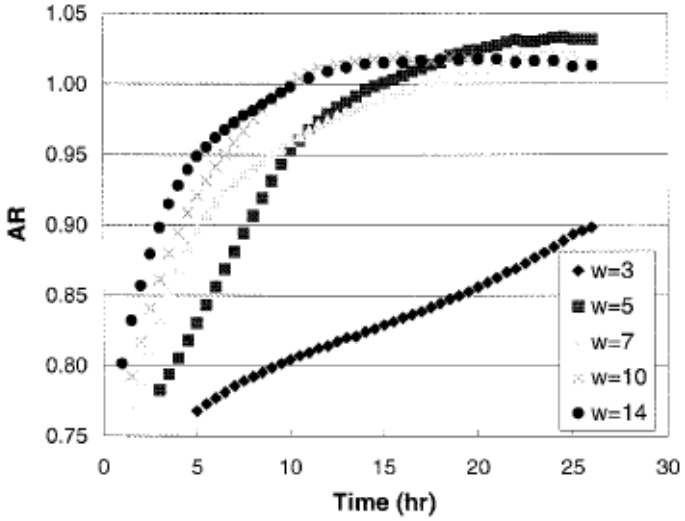


Figure 5. Comparison of copper particle growth curves in AOT reverse micelles in cyclohexane at various water contents.[47] AR is the ratio of the absorbance of the peak at 566 nm to an absorbance off the peak, in this case 500nm (as described in ref 47).

1.2.3 Particle Shape Control

Two excellent review papers[3,4] by Pileni cover extensive work on approaches to affect particle shape; indeed Pileni's group can justifiably be identified as pioneers and innovators in this field. The reviews cover the three main factors which affect particle shape; the influence of the micellar template, added anions, and molecular adsorption. More recently another facet, that of defect engineering, has been added.[53,70] As discussed below, in certain systems particle shape control has been established, however a general method for shape control of nanoparticles by the microemulsion route has yet to be found. Figure 6 shows some of the more interesting particle shapes which have been grown using water-in-oil microemulsion templates.

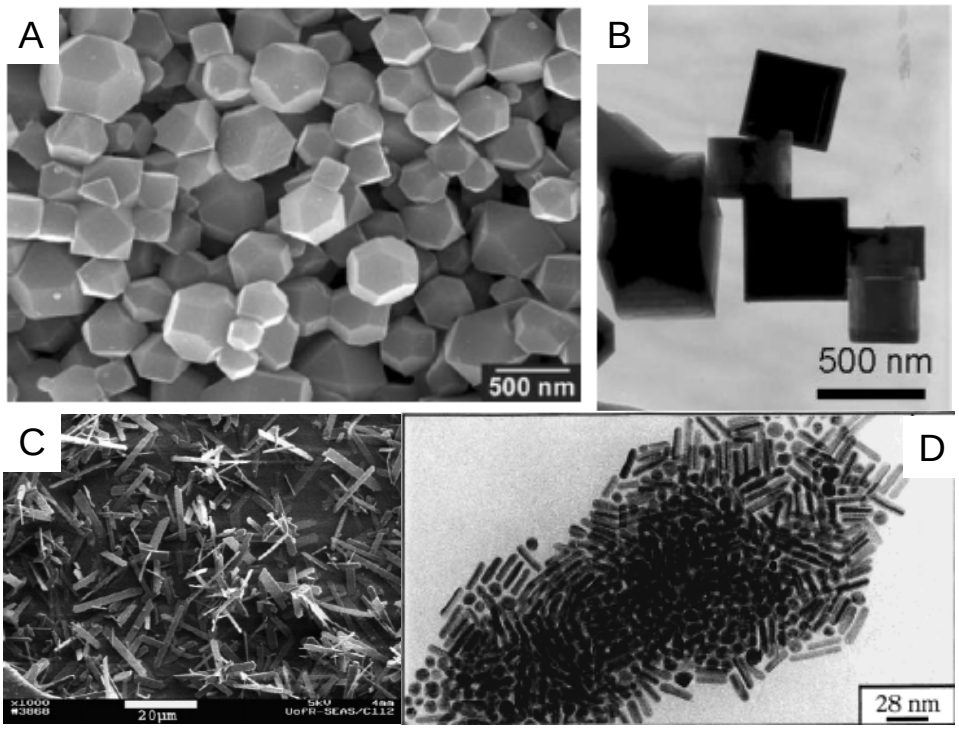


Figure 6. Shape control of nanoparticles generated in microemulsions; (A) SEM image of $Co_3[Co(CN)_6]_2$ polyhedra,[118] (B) TEM image of PbS cubes,[84] (C) SEM image of Silicalite-1 nanocrystals with coffin-morphology,[105] (D) TEM image of Cu nanorods.[58]

Effect of the micellar template

Despite plenty of work, there is still much controversial debate surrounding this area. Just as with control of particle size, many groups claim control of particle shape using micellar templates. A simple surfactant–water–oil system can produce many different self-assembly structures: by changing composition, one can obtain spheres (reverse micelles or micelles), cylinders, interconnected cylinders and planes termed lamellar phase, which also can re-organize into onion-type structures.[3,4] Hence in theory many possible nanoparticle structures could be grown inside these different shaped templates, and indeed several groups have reported such templating effects.[58,105,106,118,135] A comprehensive study has been carried out by Rees et al.,[107] in which a variety of surfactants and system compositions (e.g. surfactant and water concentrations) were investigated on the growth of a number of different nanocrystal structures. However, it has been shown that different shapes of nanoparticle can be made without changing template shape,[57] and sometimes no templating effect is seen at all.[120] One direct example is by Eastoe et al, investigating templating using polymerizable surfactants.[109] Before polymerization, there was little correlation between micelle shape and the particle shape grown, but significant shape replication was observed after polymerization. These results could be used to help with shape control in the future, however the balance of current evidence points to the initial micellar template only exerting partial control over the resulting nanocrystal shape.[3,4]

The influence of ion/molecular adsorption

These two factors have been reviewed by both Pileni and Holmberg.[4,14] Investigations have shown that the identity of anion species added as electrolyte are important for generating different shapes of copper nanocrystals.[56] The tendency is to follow the Hoffmeister series.[57] However, the initial micellar shape is shown to be largely unaffected by these additives.[55] Also for copper nanoparticle systems, a large excess of hydrazine favors disk over spherical particles. In both cases, Pileni et al. postulate that selective adsorption of molecules or ions on to facets of the nanocrystal effect growth in certain directions, explaining the apparent preference for certain shapes. Uskokvic and Drofenik present a similar argument in a study showing how the pH affects the shape of nanostructured NiZn ferrites.[117] When the pH is lower, needle-like nanocrystals are formed, whereas spheres are observed at higher pH. One possible

reason for this is due to an increased number of hydroxyl ions at higher pH which eliminate the sulphate and bromide ions, hampering their ability to promote uniaxial growth.

Defect engineering

Most recently, a new method has been proposed for control of nanoparticle shape by Pileni's group.[70] They reported synthesis of silver nanodisks with varying size, viewed by HRTEM (high resolution transmission electron microscopy). Characterization of these disks via SAED (selected area electron diffraction – see electron microscopy appendix) showed the presence of forbidden 1/3{422} reflections. This had been previously seen by other authors, with a variety of models proposed to explain the peaks. Pileni, however, proposed that these models are flawed and that it is likely to be a stacking fault in the *[111]* plane that causes these reflections. In addition, it is proposed that the existence of such a fault promotes growth in the area parallel to it, thus leading to the formation of nanodisks only. Therefore, it appears that defect design may be employed to influence the shape of nanoparticles. Encouragingly, this work was repeated with a copper system,[53] yielding similar results. Again, defects in the *[111]* plane were observed and the link between these defects and particle shape were discussed. Growth is proposed to be favored parallel to the defects, due to the presence of troughs in which both nucleation and growth are favored. This current approach appears to hold much promise for the synthesis of tailored nanodisks.

1.3 Water in sc-Fluid Microemulsions

A supercritical (sc) fluid is above both its critical temperature (T_c) and critical pressure (P_c). With sc-fluids a smooth transition in solvent quality between liquid-like and gas-like properties is possible by external control over pressure and temperature. By judicious choice of surfactant it is possible to stabilize microemulsions in sc-fluids.[17,19] This section covers use of supercritical fluids and also high pressure liquids (above critical pressure, but below critical temperature) as media for nanoparticle synthesis. Of particular interest has been liquid and sc-CO_2: the potential of sc-CO_2 as a novel green solvent has been discussed elsewhere.[17] Specifically for the synthesis of nanoparticles, the benefits are apparent; firstly by making the process more environmentally benign, and secondly facilitating the facile recovery of nanomaterials after the reaction has taken place by merely reducing the pressure and releasing the gas. A good example of the benefits of incorporating supercritical CO_2 into this process has been shown by Zhang et al.[136] Xylene is an inadequate solvent to stabilize a microemulsion of water/P104/xylene in presence of CO_2 at ambient pressure (P104: $(EO)_{27}(PO)_{61}(EO)_{27}$ where EO = ethylene oxide, PO = propylene oxide). However, at higher pressure the microemulsion becomes stable, allowing the formation of Au nanoparticles via reduction (KBH_4) of $HAuCl_4$. The gold particles were easily recovered by reducing pressure to release the solvent. The surfactant remains in the xylene phase, whilst the unstable nanoparticles precipitate out. Another technique, known as RESOLV (rapid expansion of a supercritical solution into a liquid solvent) (figure 7), where a stable microemulsion of silver cations in sc-CO_2 is expanded through a nozzle into solvent containing a reducing agent, has been used successfully to produce silver nanoparticles with good size control.[137] Finally, water in supercritical (w/sc-f) fluid microemulsions have been successfully employed, in a similar way to water-in-oil (w/o) microemulsions, in the synthesis of a variety of compounds, given in Table 2. Note that many such materials have applications in industry - silver compounds for photographic imaging or semiconductors, TiO_2, Rh, Pt in catalysis.

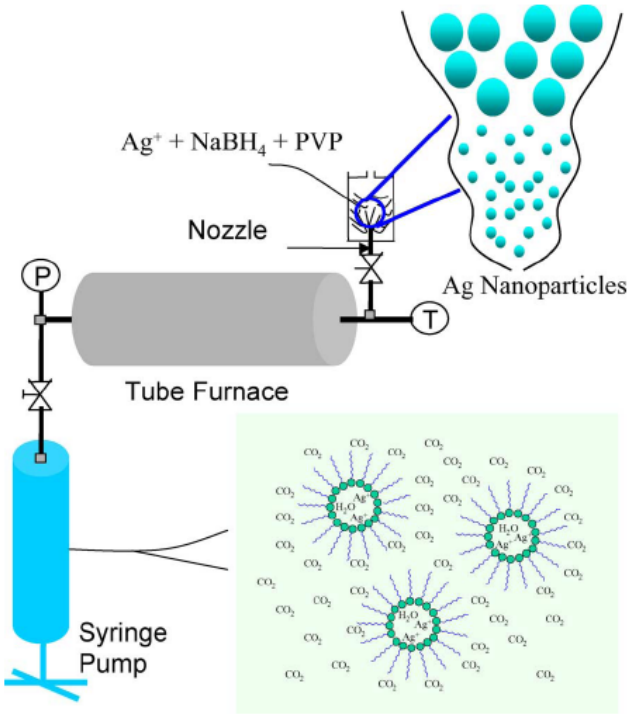


Figure 7. Experimental setup for RESOLV.[137]

Metals	Ag,[138-141] Rh,[142] Pd,[143] Cu[62,144]
Metal oxides	TiO_2,[145,146] TiO_2/SiO_2[146]
Metal sulphides/halides	CdS,[89] AgI,[139,147] AgBr,[147] AgCl,[147] Ag_2S,[148] CuS[149]

Table 2. Nano-materials formed in w/sc-CO_2 microemulsions

1.3.1 Methods

Synthesis in w/sc-f microemulsions is carried out in much the same way as in water in oil microemulsions, with slight differences. Firstly, one has to prepare a stable dispersion using appropriate surfactant(s). In w/o microemulsions, the most popular choice of surfactant is AOT and for most liquid/supercritical alkanes, AOT can still be applied.[62,138,144] However, when using liquid or supercritical CO_2, AOT will not form stable microemulsions alone, being of low compatibility with the continuous CO_2 phase (discussed in chapters 3 and 7). Fluorinated co-surfactants, such as PFPE-PO_4 (perfluoropolyether-phosphate)[141-143,147] or F-pentanol[139,148] must be employed to

stabilize the dispersions. Another popular stabilizer is the fluorinated surfactant PFPE-NH_4 (ammonium perfluoropolyether).[140] Other reviews and later chapters provide compilations of surfactant candidates for stabilizing w/sc-f microemulsions.[17,19] At the time of writing, a current "holy grail" of research is to find novel hydrocarbon-based surfactants or polymers capable of stabilizing w/sc-CO_2 microemulsions due to the extra economic and environmental benefits this would provide. Roberts et al. have come some way towards achieving this goal, reporting successful stabilization of nanoparticles (pre-fabricated in AOT-stabilized w/o microemulsions) using isosteric acid in a sc-CO_2 solvent system with approximately 10% hexane by volume added.[150]

Stable w/sc-CO_2 microemulsions may be achieved, containing polar reactants solubilized inside reverse micelles. The microemulsions must be formulated in a pressure cell; water, reactant and surfactant are added and CO_2 is distilled or pumped in. Single phase regions are accessed by increasing pressure or temperature under efficient stirring. The second reactant may be injected into the vessel using a high pressure syringe pump. Hence, the nanoparticle reactions take place in the same way to that in normal liquid w/o microemulsions, growth still being strongly dependent on intermicellar exchange. Figure 8 shows attractive images taken through pressure cell windows of Ag nanoparticle formation in a w/sc-CO_2 microemulsion.[139] Particle recovery, both by venting of CO_2,[19,139,145,148] and by other rapid expansion methods[19,141] has been successfully accomplished.

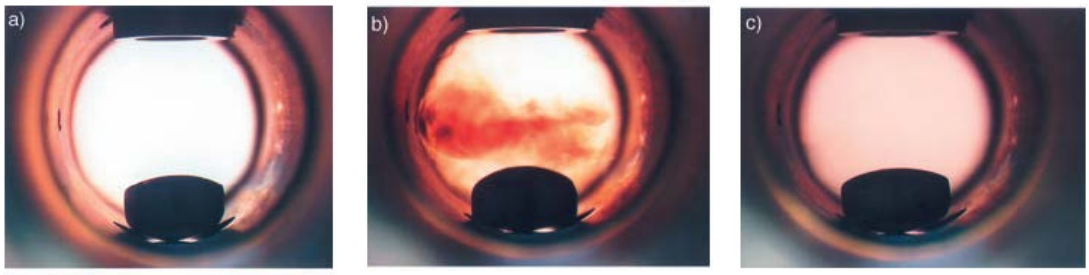


Figure 8. Formation of Ag nanoparticles in AOT and F-pentanol – stabilized water in CO_2 microemulsions: a) microemulsion before the addition of the reducing agent, b) soon after the addition of the reducing agent, and c) the optically transparent Ag nanoparticle dispersions.[139]

1.3.2 Size/shape control

The size of nanoparticles formed in w/sc-f microemulsions may be greatly affected by the template size. Liu et al. report that after nucleation, nanoparticle growth occurs to a limiting value, the size of the original water core.[19] This suggestion is supported in work by both Lim et al. and Holmes et al.[89,145] However, as with the case of w/o microemulsions, it may be that the maximum possible size depends on the ability of the microemulsion to stabilize such particles. The ability to tune the density of the solvent via changes in pressure and temperature is extremely useful in influencing intermicellar exchange and maximum size, by changing the interparticle attractions or repulsions, thus leading to greater size control than with traditional w/o microemulsions.[18,19] Research by Cason et al.,[138] both in experimental and modeling studies on the synthesis of Cu nanoparticles in compressed propane, found increasing pressure increased solvent-tail interactions, thus enabling synthesis and stabilization of larger particles than at lower pressures. Reactions were also found to be quicker in these sc-f solutions than similar reactions in w/o microemulsions.

Control of the morphology of synthesized particles is still a very new area. However, work by Kitchens et al.[62] on formation of copper nanoparticles in compressed propane found that the addition of chloride ions (HCl) induced the formation of extremely stable diamond shaped assemblies (Figure 9). Furthermore, it was demonstrated to be exclusive to the sc-f continuous system. Given the reported effects of anion addition for the control of the shape of nanoparticles in w/o microemulsions,[4,14] this could also be a promising area for further research into morphological control in these sc-f systems.

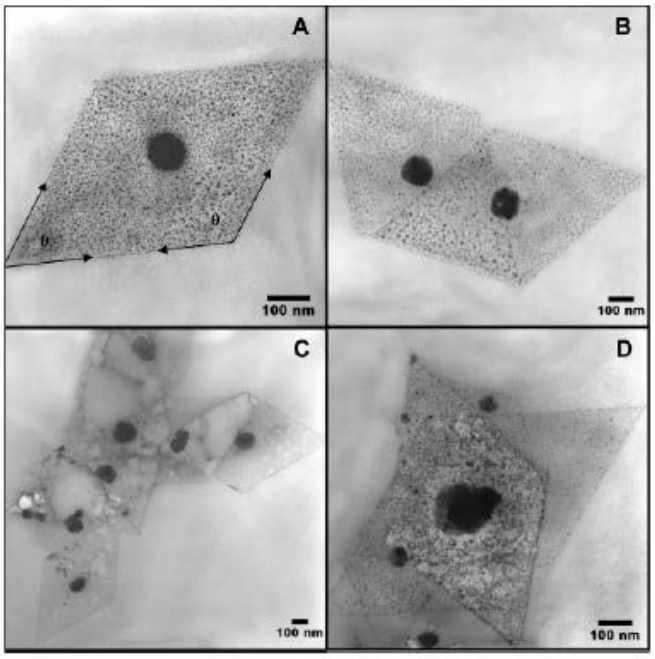


Figure 9. TEM images of diamond shaped assemblies of copper nanoparticles synthesized in compressed propane/AOT-$Cu(AOT)_2$/ w=3 reverse micelles with [HCl] = 4.2 $x10^{-2}$ mol dm^{-3} within the micelle core.[62]

1.4 Conclusions

A large number of different nano-materials have been synthesized in water-in-oil microemulsions and reversed micelles. Particle growth has shown to be strongly dependent on inter-micellar exchange rates. The resultant particle size appears to be dependent on five dominant parameters:

- solvent type
- surfactant/co-surfactant type
- concentration of the reagents
- ionic additives
- composition via [water]:[surfactant] ratio, w_0

Particle shape has been altered by three different methods; either by changing the micellar template shape, by defect engineering or by preferential absorption of species onto facets. However, this has so far been confined to specific examples and the generality of these effects remain to be established.

Water-in-supercritical fluid (or compressed liquid) microemulsions have some benefits, particularly in the extra control from solvent tunability. From a Green Chemistry viewpoint, the use of supercritical CO_2 is particularly interesting, especially if hydrocarbon surfactant candidates capable of stabilizing both nanoparticles in sc-CO_2 and w/sc-CO_2 microemulsions are found. The facile nature of collecting particles synthesized by this method, by carefully venting the CO_2 solvent, or other rapid expansion techniques, holds much promise for high volume generation and recovery of nanoparticles for potential commercial applications.

1.5 Significant recent highlights

As briefly mentioned in section 1.1, the above review was compiled in the final quarter of 2005. Since that date, a further 1333 manuscripts have been published on the subject of "nanoparticles", "synthesis" and "microemulsions" (a search for these keyword on Scifinder Scholar database on 12/03/2009 gave 2554 hits), representing a doubling in field literature volume. Much of this work is derivative, focusing on the formation of a range of different materials using the same general method, which whilst of interest (where the nano-material could be of practical use) is nevertheless out of scope for this chapter. With respect to the areas of interest outlined in this thesis however, there have been some major advances.

One such advance concerns silver nanoparticle (Ag-NP) synthesis in scCO_2 with fluorine-free ligands,[151] which builds on the already significant report of nanoparticle stabilization in scCO_2 by the same group.[150] This new work uses the CO_2-phillic surfactant AOT4, developed by the Eastoe group[152-154] (described in the paper as “AOT-TMH” and discussed in more detail in chapters 2, 3 and 7). The Na^+ cation of AOT4 was exchanged for Ag^+, which was subsequently reduced by the addition of $NaBH_4$ dissolved in ethanol (resulting in approximately 0.6 vol% ethanol) in the presence of the CO_2-phillic isostearic acid,[150] in scCO_2 to form a stable dispersion of Ag-NPs. Any potential application of NP-dispersions in sc-CO_2 is likely to require the addition of organic species (as reactants) so the addition here of a relatively small quantity of ethanol (shown previously to increase solubility of solutes in CO_2)[155] is hardly significant. This work is therefore groundbreaking, although given the complex nature

of the system, and the addition of ethanol there is still room for further developments, such as those discussed in chapters 4 and 7.

One of the most clear application fields (other than established applications in pigmentation, detergency and printing) for NPs is in catalysis. A recent review by one of the founders of microemulsion-based NP synthesis details advances in this field.[156] However, there are significant problems with such applications; in order to prepare the NPs, impurities (e.g. stabilizing ligands and reductants) must be introduced into the system, often in large excess. Such impurities are known to have adverse influence on NP properties with relation to reactivity and stability; therefore for successful applications, highly pure systems will be required.[157] Existing NP purification techniques (e.g. centrifugation) often suffer from the disadvantages of being time consuming and highly energy or solvent intensive and often inefficient in removing all salt and small-molecule impurities.[157] This therefore represents an important new area of study for nanotechnologists. Some advances have been made, e.g. precipitation by anti-solvent,[79,136,158] flocculation by use of a photolyzable surfactant[76,159] or temperature induced separation,[160,161] but at the time of writing this remains a young field and interesting developments can be anticipated.

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