Recent advances in nanoparticle synthesis with reversed micelles

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Abstract

Synthesis of nanoparticles in microemulsions is an area of considerable current interest. This subject can be broadly divided into two sections defined by the nature of the host microemulsion reaction medium.

Water-in-oil microemulsions have been used to prepare nanoparticles for more than two decades, and a wide variety of materials has been synthesised by these methods. Control parameters have been elucidated for influencing both nanoparticle concentration and morphology, allowing for tailored syntheses with various applications.

More recently, the ability to synthesise nanoparticles in water/supercritical fluid microemulsions was realised. This method promises to be a highly useful route for controlled nanoparticle synthesis due to the added control variables afforded by tuneability of the solvent quality (density) through pressure and temperature.

This review presents the current state-of-the-art in both fields.

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Keywords: Nanoparticles; Nanoparticle synthesis; Reversed micelles; Microemulsions; Supercritical fluids

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1. Introduction

Nanoparticle synthesis in microemulsions has been a hot research topic since the early 1980s, when the first colloidal solutions of platinum, palladium and rhodium metal nanoparticles were prepared [1]. Since this groundbreaking work, a huge variety of nanoparticles has been synthesised, in both water-in-oil and water-in-supercritical fluid microemulsions. A database search conducted for the preparation of this article revealed 1221 references containing 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. This review aims to summarise the most recent work, as well as discussing the current state of understanding about control over nanoparticle morphology and dimensions. Of special interest is the design and synthesis of nanoparticles with specific properties for advanced applications.

2. Water in oil microemulsions

A microemulsion is a thermodynamically stable dispersion of two immiscible fluids; the system is stabilised 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-CO2 (w/sc-CO2). A “water-in-oil” 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 dispersed in a hydrocarbon based continuous phase diagram (Fig. 1). In this region, thermodynamically driven surfactant self-assembly generates aggregates known as reverse or inverted micelles (L2 phase on Fig. 1) [22]; spherical reverse micelles, which minimise surface energy, are the most common form. Added polar or ionic components will become compartmentalised into the central cores of these reversed micelles, hence affording fine dispersion of inorganic materials in oil. It is important to recognise 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 [23,24]. Clearly, any inorganic reagents encapsulated inside the micelles will become mixed. This exchange process is fundamental to nanoparticle synthesis inside reversed micellar ‘templates’, allowing different reactants solubilised in separate micellar solutions to react upon mixing. Micelles in these systems can be described as “nanoreactors”, providing a suitable environment for controlled nucleation and growth. In addition, at the latter stages of growth, steric stabilisation provided by the surfactant layer prevents the nanoparticles from aggregating [6].

Nanoparticles have been synthesised employing this method for a variety of novel applications; topical examples include catalysts for fuel cells [25,26], food applications [27], nanorobes for fluorescent bioassays [28], novel nanofluids [29] and uses in dechlorinating chlorinated olefins [30]. Other preparations have employed novel biocompatible microemulsions [31], environmentally safe systems [32,33], including high-efficiency silicone surfactants [34,35]. More complex syntheses have also been reported, including mixed Co/Ag [36] nanoparticles, microemulsions containing monomer and initiator to form nanoparticles constrained inside a polymer matrix [37] and nanotube-containing microemulsions for generating carbon nanotube/polyaniline composites. However, probably one of the most adventurous examples is the bio-mimetic “emergence” work by the Mann et al. [38–44]. Several extremely complex nanostructures have been made and superbly imaged by this group, demonstrating that this relatively straightforward method may have important applications.

2.1. Synthetic methods

The most widely used approach is shown in Fig. 2. This involves the preparation of two separate microemulsions, 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 by Li et al. [45] provides insight into the process. Fig. 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 10 μs–1 ms [6] — slow compared to diffusion of reagents inside the polar domains), as previously concluded by several articles and reviews [6,9]. It is important to note that this has repercussions for reaction rates — the time taken for a reaction to go to completion in reversed micellar media is vastly different from the native aqueous solution [46]. Control of this exchange, via interfacial fluidity of the surfactant membrane, is believed to be a significant factor. Note that successful use of this method has also been achieved with three separate microemulsions, mixed together to produce BaTiO3 [47].

Another method to synthesise nanoparticles is from a single microemulsion. One of the desired reactants is solubilised inside reverse micelles, and a second reactant (often a reductant) added directly to the system. This is a common way to produce metal...
nanoparticles. Table 1 presents a compilation of nano-materials formed using either of these methods.

Despite this large number of successes, it is not always possible to synthesise 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 [78], 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. Vera et al. [104,105] report direct reaction of silver metal solubilised in reverse micelles with the surfactant (dioctyldimethylammonium halide) counter-ion to prepare silver halides. Shen et al. [106] employed gamma irradiation of a micellar solution of copper nitrate to form copper metal which is then oxidised in situ to cuprous oxide. In these cases, intermicellar exchange has less of an influence on the final outcomes (size, polydispersity, shape), providing faster rates and new possibilities for morphological control.

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 \( w_0 = \frac{[\text{water}]}{[\text{surfactant}]} \).

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 \( \kappa \), \( K \) or "\( 2K + K\text{Bar} \)". Szleifer et al. [107] employed the Helfrich formula (given elsewhere [108]) 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 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 [108–110]. The effect of different solvents has also been studied [108,110], and found to be of second order when compared to the points mentioned above. The type of solvent only produces noticeable differences in rigidity for large changes in chain length.

2.2.1. Solvent effects

Particle size is affected by solvent type. This was shown initially by Pilieni et al. in a study on silver nanoparticles [67], in which larger particles were seen (by TEM) to be formed in isooctane than in cyclohexane. A significant difference in intermicellar exchange rate constant between the two solvents — a factor of 10 [111] has previously been reported. Bagwe and Khilar [85], and then Cason et al. [46] investigated this effect in various systems (AgCl, Cu), both showing that different solvents affect particle growth rate, final size and polydispersity. However they found cyclohexane gave larger particles when the system was left for very long time periods (Pileni et al. were unable to do this as their system aggregated after 1h). Kitchens et al. corroborated these results in a rigorous modelling study [58].

The change in growth rate has been explained in the following way: smaller, less bulky solvent molecules with lower molecular volumes, such as cyclohexane, can penetrate between

![Fig. 2. Proposed mechanism for the formation of nanoparticles by the microemulsion approach. Reprinted from [11] with permission from Elsevier.](image1)

![Fig. 3. TEM images of ZnSe particle growth in reverse micelles. Aging times: (A) 5 min; (B) 30 min; (C) 2 h; (D) 12 h after initiation of the reaction. Reprinted from [45] with permission from Elsevier.](image2)
surfactant tails, increasing “surfactant curvature and rigidity” [46]. As previously discussed, this increased rigidity at the interface may lead to a slower growth rate. Isooctane, being bulkier with a larger molecular volume, cannot penetrate the interface may lead to a slower growth rate. Isooctane, being bulkier with a larger molecular volume, cannot penetrate the interface and thus faster growth rates. Although these ideas provide plausible explanations of the phenomena they remain controversial. Measurement of the surfactant film rigidities in microemulsions show that the solvent type has only a minor effect [108,110]. Solvent molecular volume may also 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 stabilise larger particles” [6]. Any increase in rate of intermicellar exchange will 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 by Ganguli et al. [79] 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 iso-octane (higher molecular volume).

### 2.2.2. 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-dodecyl dimethylammonium bromide (DDAB) and non-ionic 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 [6,9]. 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 functionalising with a metal ion partaking in the nanoparticle-producing reaction, by substitution of the sodium ion, can improve monodispersity [3].

### Table 1

<table>
<thead>
<tr>
<th>Metalloids/Alloys</th>
<th>Pt [1,25], Rh [1], Pd [1], Cu [20, 46, 48–58], Co [59–62], Ag [62–67], Au [68, 69], Ni [70]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semiconductors</td>
<td>ZnS [32, 71], PbS [72], CdS [73–77], CdTe [78], ZnSe [45], Ce–Tb and Ce–Zr [26]</td>
</tr>
<tr>
<td>Metal oxides/halides</td>
<td>CuO [55, 79], ZrO2 [80], CeO2 [81], TiO2 [82, 83], AgCl [84, 85]</td>
</tr>
<tr>
<td>Other inorganic compounds</td>
<td>Ca(OH)2 [86], CaCO3 [86, 87], silicate-1 [88], Ca3(PO4)2 [33, 40, 89], CaSO4 [90], BaSO4 [90, 91]</td>
</tr>
<tr>
<td>Magnetic compounds</td>
<td>Fe3O4 [90, 92], Fe2O3 [93, 94]</td>
</tr>
<tr>
<td>More complex (for applications)</td>
<td>SrRu2O4 Eu1+ where R=Y, Lu [95], YF3 [96], BaZrO3 [97], Eu2O3 [98], NiZn ferrite (NiO, ZnO, Fe3O4, O3,S) [99], Prussian blue [100], Fe-Cu-B alloys [10]</td>
</tr>
<tr>
<td>Polymers</td>
<td>Polyacrylamide [102], poly(alkylacrylatedic acid) [103]</td>
</tr>
</tbody>
</table>

This must be done carefully as counterion exchange can have significant effects on the stability of reversed micelles [112]. In addition, the shape of the micellar aggregates is also known to be strongly affected by the nature of the counterion [113].

An interesting study, carried out by Lee et al. [82], investigated the effect of surfactant structure on size of TiO2 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 favoured by both smaller head groups and shorter tails. The authors theorise 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 1 h. As previously discussed, longer hydrophobic chains may lead to a more rigid interface [107–110], 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 should lead to more rigid films and therefore smaller particles).

The effect of different surfactants has also been investigated by Zaki et al., in which nanometre sized nanocrystals of CeO2 were synthesised with a wide range of surfactants [81]. They found the resultant nanoparticles have different shapes, sizes and stabilities. Work carried out by Spirin, Brichkin and Razumov reported that Triton X100 to be a much more suitable surfactant in the synthesis of gold nanoparticles than AOT. It has therefore been shown by various studies that the choice of surfactant is critical to the size, shape and stability of the particles.

Lopez-Quintela et al. [6] and Uskokovic [9] have both reviewed the effect of co-surfactant on the final particle size. 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 [107, 108]. The effects of changing co-surfactant structure have recently been explored by Charipanikutik et al. [71] and it appears that a decrease in particle size is observed when the co-surfactant chain length is shortened.

### 2.2.3. Added electrolyte

Work has been carried out by both Kitchens et al. [56] and Saiwan et al. [83] following the effects of added salt on eventual particle size. 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 destabilisation of the micellar system. A summary of work in this area can also be found in the review by Uskokovic and Drofenik [9].

2.2.4. Reagent concentration

Several studies [60,62,63,93,94] have shown an increase in particle size goes hand-in-hand with reactant concentration. The clearest example is from the work of Pileni et al. [63], who investigated the size of silver nanodisks generated as a function of the concentration of added reducing agent (hydrazine). As the ratio [hydrazine]:[AOT] was increased, an increase in particle size was observed, leading to changes in optical properties of the nanoparticle dispersion (Fig. 4). A similar increase in particle size with ratio [hydrazine]:[AOT] was observed by Eastoe et al. [62] for the case of colloidal cobalt. One plausible explanation is that a ‘polymerisation’ of AOT occurs via reaction with hydrazine to form an imine dimer, previously shown by Clint et al. [114].

Increasing reagent concentration also appears to reduce polydispersity. In studies by both Pileni et al. [60] and Eastoe et al. [72], an increase in the number of particles of a similar size were noted when concentration of reagents, NaBH₄ and PbS respectively, was raised.

2.2.5. Water content

This effect has been reviewed extensively elsewhere [2–9,11,13,16]. However, confusingly these papers tend to arrive at different conclusions. In most papers, water content is described by the water to surfactant molar ratio, \( w_0 = [\text{H}_2\text{O}]/[\text{surfactant}] \), however it is important to recognise 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 [84]. 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 \( w_0 \) [7,20,34,57,70,76,77,84,86,92,94,96,115–117], demonstrating control over the outcomes of the syntheses merely by changing \( w_0 \). It is also generally observed that the size of the nanocrystals produced differs from that of the initial nanoreactors, and also the variation in particle size with \( w_0 \) 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 [118,119]. Unfortunately in many cases, the same effect is not seen [6,8,9,13,46,58,62,72,103].

Cason et al. [46] and then Kitchens et al. [58] found that, at any given value of \( w_0 \), the same size nanoparticles can be synthesised if left for sufficient time for the reaction to go to completion (Fig. 5). They proposed that the rate of nanoparticle growth is affected by varying \( w_0 \). 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 [7]. With the water bound, the micelle interface is said to be “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 \( w_0 = 10–15 \) [85,116]). 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 [85]. These ideas and findings run contrary to the bulk of other work [7,20,34,57,70,76,77,84,86,92,94,96,115–117] which suggest that particle size can indeed be controlled by \( w_0 \).

2.3. Particle shape control

Two excellent review papers by Pileni [2,3], cover extensive work on approaches to affect particle shape. Pileni’s group can justifiably be identified as pioneers and innovators in this field. These reviews cover the three main factors which affect particle shape; the influence of the micellar template, added anions, and molecular adsorption. More recently, another factor of defect engineering has been added [48,65]. 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. Fig. 6 shows some
of the more interesting particle shapes which have been grown using water-in-oil microemulsions.

2.3.1. 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 phases, which also can re-organise into onion-type structures [2,3]. Hence in theory many possible nanoparticle structures could be grown inside these different shaped templates, and indeed several groups have reported such templating effects (A, C, D on Fig. 6) [53,88,89,100,121]. A comprehensive study has been carried out by Rees et al. [90], in which a variety of surfactants and system compositions (surfactant/water concentrations) was 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 [52], and sometimes no templating effect is seen at all [103]. One direct example is by Eastoe et al., investigating templating using polymerisable surfactants [91]. Before polymerisation, there was little correlation between micelle shape and the particle shape grown, but significant shape replication was observed after polymerisation. 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 a partial control over the resulting nanocrystal shape [2,3].

2.3.2. The influence of ion/molecular adsorption

These two factors have been reviewed by both Pileni [3] and Holmberg [13]. Investigations have shown that the identity of anion species added as electrolyte is important for generating different shapes of copper nanocrystals [50]. The tendency is to follow the Hoffmeister series [51]. However, the initial micellar...
shape is shown to be largely unaffected by these additives [52]. Also for copper nanoparticle systems, a large excess of hydrazine favours disk over spherical particles. In both cases, Pileni et al. postulate that selective adsorption of molecules or ions on to facets of the nanocrystal affects 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 [99]. 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.

2.3.3. Defect engineering

Most recently, a new method has been proposed for control of nanoparticle shape by Pileni’s group [65]. They reported synthesis of silver nanodisks with varying size, viewed by HRTEM (high resolution transmission electron microscopy). Characterisation of these disks via SAED (selected area electron diffraction) 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 [48], yielding similar results. Again, defects in the \([111]\) plane were observed and the link between these defects and particle shape was discussed. Growth is proposed to be favoured parallel to the defects, due to the presence of troughs in which both nucleation and growth are favoured. This current approach appears to hold much promise for the synthesis of tailored nanodisks.

3. Water in supercritical 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 stabilise microemulsions in such solvents [18,21]. This section covers use of sc-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 supercritical CO₂: the potential of sc-CO₂ as a novel green solvent has been discussed elsewhere [21]. Specifically for the synthesis of nanoparticles, the benefits are apparent; firstly by making the process more environmentally benign, and secondly facilitating the recovery of nano-material after the reaction has taken place by merely reducing the pressure and releasing the gas. A good example of the benefits of incorporating supercritical CO₂ into this process has been shown by Han et al. [122]. Xylene is an inadequate solvent to stabilise a microemulsion of water/P104/xylene in presence of CO₂ 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 (KBH₄) of H₂AuCl₄. 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) (Fig. 7), where a stable microemulsion of silver cations in sc-CO₂ is expanded through a nozzle into solvent containing reducing agent, has been used successfully to produce silver nanoparticles with good size control [123]. Finally, water-in-supercritical fluid (w/sc-fluid) 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, TiO₂, Rh, Pt in catalysis.

### 3.1. Methods

Synthesis in w/sc-fluid microemulsions is carried out in much the same way as in w/o microemulsions. 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 [56,124,130]. However, when using liquid/sc-CO₂, AOT will not form stable microemulsions alone, being of low compatibility with the continuous CO₂ phase. Fluorinated co-surfactants, such as PFPE-PO₄ (perfluoropolyether-phosphate) [127–129,134] or F-pentanol [125,135] must be employed to stabilise the dispersions. A popular stabiliser is the fluorinated surfactant PFPE-NH₄ (ammonium perfluoropolyether). Other reviews provide compilations of surfactant candidates for stabilising w/sc-fluid microemulsions [18,21]. A current “holy grail” of research is to find hydrocarbon-based surfactants or polymers capable of stabilising w/sc-CO₂ microemulsions due to the extra economic and environmental benefits this would provide. Roberts et al. [136] have come some way towards achieving this goal, reporting successful stabilisation of nanoparticles (synthesised in AOT-stabilised w/o microemulsions) using iso-steric acid in a sc-CO₂ solvent system with ~10% hexane by volume added.

Stable w/sc-CO₂ 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 then CO₂ is distilled or pumped in: the single phase regions are accessed by increasing pressure 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. Fig. 8 shows example images of microemulsions during Ag nanoparticle formation [125]. Particle recovery, both by venting of CO₂ [18,125,131,135], and by other rapid expansion methods [18,127] has been successfully accomplished.

### Table 2

<table>
<thead>
<tr>
<th>Nano-materials formed in w/sc-CO₂ microemulsions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metals</strong></td>
</tr>
<tr>
<td>Ag [124–127], Rh [128], Pd [129], Cu [56,130].</td>
</tr>
<tr>
<td><strong>Metal oxides</strong></td>
</tr>
<tr>
<td>TiO₂ [131,132], TiO₂/ SiO₂ [132].</td>
</tr>
<tr>
<td><strong>Metal sulﬁdes/halides</strong></td>
</tr>
<tr>
<td>CdS [133], AgI [125,134], AgBr [134], AgCl [134], Ag₂S [135]</td>
</tr>
</tbody>
</table>

Stable w/sc-CO₂ 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 then CO₂ is distilled or pumped in: the single phase regions are accessed by increasing pressure 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. Fig. 8 shows example images of microemulsions during Ag nanoparticle formation [125]. Particle recovery, both by venting of CO₂ [18,125,131,135], and by other rapid expansion methods [18,127] has been successfully accomplished.
3.2. Size/shape control

The size of nanoparticles formed in w/sc-fluid 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 [18]. This suggestion is supported in work by both Lim and Hwang [131] and Holmes et al. [133]. 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 stabilise such particles. The ability to tune solvent density via changes in pressure and temperature is extremely useful in influencing intermicellar exchange and maximum size, by changing the inter-particle attractions/repulsions, thus leading to greater size control than with traditional w/o microemulsions [17,18]. Research by Cason et al. [124], both in experimental and modelling studies on the synthesis of Cu nanoparticles in compressed propane, found increasing pressure increased solvent-tail interactions, thus enabling synthesis and stabilisation of larger particles than at lower pressures. Reactions were also found to be quicker in sc-fluid solutions than similar reactions in w/o microemulsions.

Control of the morphology of synthesised particles is still a very new area. However, work by Kitchens et al. [56] 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 (Fig. 9). Furthermore, it was demonstrated to be exclusive to the sc-fluid continuous system. Given the reported effects of anion addition for the control of the shape of nanoparticles in w/o microemulsions [3,13], this could also be a promising area for further research into morphological control in these sc-fluid systems.

4. Conclusions

A large number of different nano-materials have been synthesised in water-in-oil microemulsions and reversed micelles. Particle growth has shown to be strongly dependent on intermicellar 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 [2,3,53,88,89,90,100,116], by defect engineering [48,65] or by preferential absorption of species onto facets [3,13,50–52,99]. However,
this has so far been confined to specific examples and the generality of these effects remains to be established.

Water-in-supercritical fluid (or compressed liquid) microemulsions have some benefits, particularly in the extra control from solvent tunability. From a viewpoint, emulsions have some benefits, particularly in the extra control expansion techniques, holds much promise for high volume generation and recovery of nanoparticles for potential commercial applications.

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References
