Design of anisotropic nanostructures using microemulsions

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Water-in oil microemulsions can be intelligently designed to form organized assemblies which can then be used as nanoreactors for synthesizing a variety of nanomaterials. The size and morphology of the desired product is controlled by manipulating the parameters involved in the formation of a microemulsion like Wo ([H\textsubscript{2}O]/[Surfactant]), and the nature of solvent, surfactant and co-surfactant. This review focuses on understanding the controlled growth of anisotropic nanostructures using microemulsions emphasizing on the recent contributions by our group on synthesis of nickel and copper oxalate nanorods and silica nanostructures. We believe that this review will espouse the ability of the microemulsion method to control the shape and size of nanostructures.

**Keywords:** Microemulsions, Nanomaterials, Anisotropic nanostructures

Nanomaterials have triggered enormous interest among scientists due to the large number of unusual properties and applications associated with them. The interdisciplinary nature of the subject leads to cross fertilization of ideas between science and engineering and also between varied subjects like biology and mechanical engineering, chemistry and physics, physics and electrical energy and in many cases an overlap of three or more classical disciplines. An example of making a biological sensor will require experts of medicine, chemistry, physics, mechanical and electrical engineering or electronics. However, a large part of current research is to synthesize suitable nanostructures with well defined composition, size and morphology. Among nanomaterials, anisotropic nanostructures (nanorods, nanofibres and nanowires) are especially important and this is a challenging area with potential applications in nanodevices. Controlling the size and shape of nanostructures requires methodologies where there is scope to vary the reaction parameters.

The microemulsion method has advantages over other synthetic methodologies due to the control over homogeneity, final stoichiometry and particle size of the nanoparticles. The main constituents required to form a microemulsion are the surfactant, co-surfactant, oil/non-polar phase and aqueous solution. These form tiny aqueous droplets (nanodimensions) and are dispersed homogeneously throughout the microemulsion. These aqueous droplets are used as nanoreactors to synthesize materials with particle size in the range of 4-50 nm size. The main advantage of this method is that the product formed is homogeneous and monodispersed. The morphology of the product may be varied through proper choice of the surfactant aggregates. A number of parameters are involved that control the size and shape of the surfactant aggregates formed in the microemulsion. These include Wo ([water]/[surfactant]), surfactant packing parameter, nature of non-polar phase (oil), surfactant, etc. Due to the involvement of several variables (surfactant, co-surfactant, solvent, amount of water, temperature) it is possible to fine-tune the composition of the microemulsion, and hence, the size and shape of the reverse micelle.

We have used water-in-oil microemulsions called reverse micelles for the synthesis of nanomaterials. In this, the polar head of the surfactant molecules are directed towards the core (being polar) and the hydrophobic tail points towards the non-polar solvent. There have been several reports on the formation of anisotropic nanostructures using reverse micellar methods such as 1D SnO\textsubscript{2} nanocrystals\textsuperscript{1}, nanotubes of silica\textsuperscript{2}, nanotubes and nanodisks of silica\textsuperscript{3}, nanorods of Bi\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}\textsuperscript{4}, nanorods and nanodisks of copper ferrite\textsuperscript{5} and calcium ruthenate (CaRuO\textsubscript{3})\textsuperscript{6}.
In this review we discuss the role of reverse micelles and the parameters involved in the synthesis of anisotropic nanostructures. We also discuss the contribution made by our group in the field of synthesis of anisotropic nanostructures using microemulsions and show that by judiciously varying the parameters involved in the formulation of a microemulsion such as nature of surfactant, co-surfactant, solvent and the aqueous content \((W_o)\), the shape and size of the nanostructures can be controlled. The other factors which affect the growth of particles in reverse micelles are presence of additives like alcohols, electrolytes and, block copolymers, nature of continuous oil phase and reactant concentration. There have been several important reviews published on related aspects of nanomaterial synthesis using microemulsions especially during 1993–2006 by Pileni, Eastoe, Lopez-Quintela, Capek, Holmberg, and Uskokovic in 2010.

**Role of Solvent**

Nature of solvent affects the curvature and flexibility of the reverse micelles. The extent of interaction between the surfactant tails and the solvent decreases as the chain length increases and thus penetration of the solvent molecules between the surfactant chains becomes difficult. There is an increase in the inter-droplet tail-tail interaction between two surfactant molecules because of the weak presence of solvent molecules in the tail region of the droplet. Hence, an increase in the chain length of the alkyl group in the solvent results in an increase in the micellar exchange rate. This effect was shown by Cason et al. where the authors observed an increase in the curvature and decrease in the flexibility by the penetration of solvent molecules between the surfactant tails in water-in-oil microemulsions.

We have used two different solvents, viz., (a) hexane and (b) cyclohexane instead of iso-octane (used for the synthesis of nickel oxalate nanorods by Ahmad et al.) to understand the role of the solvent on the size and shape of the nickel oxalate rods. The other components (surfactant: CTAB, co-surfactant: 1-butanol) of the microemulsion was kept constant. We observed nanorods of nickel oxalate with an average diameter of 110 nm and average length of 565 nm (aspect ratio 5:1) (Fig. 1a) and average diameter of 300 nm and length of ~1.8 μm (aspect ratio 6:1) (Fig. 1b) using n-hexane and cyclohexane as the solvent respectively. Our earlier studies showed that when iso-octane was used as the non-polar solvent for the synthesis of nickel oxalate, much larger rods with diameter of 225 nm and length of ~2.5 μm (aspect ratio of 11:1) were formed. This change can be explained by the changes in the attractive interactions between the micelles which governs the intermicellar exchange rate of the reactants. Towey, Khan-Lodhi & Robinson reported in 1990 that when the solvent is changed from iso-octane to cyclohexane, the micellar exchange is decreased by a factor of 10. We observed an increase in the length and aspect ratio of the nanorod of nickel oxalate with increase in the bulkiness of the solvent molecule (i.e. \(n\)-hexane < cyclohexane < iso-octane). A bulky solvent results in an increase in the collision frequency and intermicellar exchange rate as a bulky solvent has more difficulty in penetrating and solvating the surfactant tails. This leads to an increase in the particle growth rate and consequently larger size of the particles.

**Role of Surfactant**

Variation in the surfactants is one of the important parameters of the reverse micellar system which may affect the morphology of the product synthesized using the reverse micelles. This was shown by Yang et al., wherein they synthesized quasi-nanospheres, nanoshuttles, nanowires and nanotubes of CdS by using surfactants like Tween-80, Peregals, C12E9 and Triton X-100 respectively. The different morphology was attributed to the shape of the reverse micelles formed using the surfactants, for instance, Tween-80 formed circular shaped micelles, Peregals formed elongated shaped template, wire shaped reverse micelles were formed using C12E9 while tubular shaped reverse micelles were formed with Triton X-100 as the surfactant. Thus, the initial template formed in the reverse micelles using different surfactants affects the morphology of the product.

We have also investigated the role of the surfactant on the nature of the products like nickel oxalate, copper oxalate and silica. It was observed that cationic surfactants (cetyl trimethylammonium-bromide, CTAB) resulted in the formation of nanorods for both nickel (Fig. 1(a & b)) and copper oxalate (Fig. 1(c, d & e)) while nanospindles of silica of diameter ~100 nm and length ~200-300 nm (Fig. 1f) were formed. The results have been shown in Table 1. A neutral surfactant (non-ionic) such as Tergitol and TX-100 leads to the formation of cubes for nickel oxalate with dimension of 50 nm in the case of Tergitol (Fig. 2b) whereas spherical particles of size ~5 nm were formed using TX-100 (Fig. 2c). Similarly, in the
Fig. 1—Nickel oxalate nanostructures synthesized using (a) CTAB/1-butanol/n-hexane and (b) CTAB/1-butanol/cyclohexane. Copper oxalate nanostructures synthesized using (c) CTAB/1-butanol/cyclohexane, (d) TTAB/1-butanol/iso-octane and (e) CPB/1-butanol/iso-octane. Silica nanostructures synthesized using (f) CTAB/1-butanol/iso-octane.

Table 1—Nanostructures synthesized using microemulsions with different surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Solvent</th>
<th>Silica Description</th>
<th>Nickel Oxalate</th>
<th>Copper Oxalate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB</td>
<td>Iso-octane</td>
<td>Spindles 100 (d) 200-300 (l)</td>
<td>Nanorod 225 (d) 2500 (l)</td>
<td>Nanorods 130 (d) 480 (l)</td>
</tr>
<tr>
<td></td>
<td>n-hexane</td>
<td>-</td>
<td>Nanorod 110 (d) 565 (l)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Cyclohexane</td>
<td>-</td>
<td>Nanorod 300 (d) 1800 (l)</td>
<td>Nanorods 200 (d) 600 (l)</td>
</tr>
<tr>
<td>TTAB</td>
<td>Iso-octane</td>
<td>-</td>
<td>-</td>
<td>Nanorods 150 (d) 400 (l)</td>
</tr>
<tr>
<td>CPB</td>
<td>Iso-octane</td>
<td>-</td>
<td>-</td>
<td>Nanorods 500 (d) 750 (l)</td>
</tr>
<tr>
<td>TX-100</td>
<td>Cyclohexane</td>
<td>Spherical particles 5</td>
<td>-</td>
<td>Nanocubes 60-80</td>
</tr>
<tr>
<td>Tergitol</td>
<td>Cyclohexane</td>
<td>Spherical particles 35-40</td>
<td>Cubes 50</td>
<td>Nanocubes 50-60</td>
</tr>
</tbody>
</table>
case of copper oxalate, nanocubes (of ~ 50-60 nm with Tergitol (Fig. 2e) and ~60-80 nm with TX-100 (Fig. 2f)) were formed. These results are in contrast to the nanorods obtained using cationic surfactants for nickel and copper oxalate. However, in the case of silica with the neutral surfactant, Tergitol, spherical particles were obtained with size ~ 35-40 nm (Fig. 2h). In order to figure out the mechanism of formation of rods with cationic surfactants, zeta potential studies were carried out on nickel oxalate, copper oxalate and silica nanostructures. The surface charge (obtained by zeta potential measurements on nickel oxalate nanorods) was found to be negative. A negative value (-14.3 mV) of zeta potential studies was obtained on copper oxalate synthesized in absence of surfactant (CTAB), while a positive value for zeta potential (1.8 mV) was observed for copper oxalate synthesized in presence of cationic surfactant. A value of -29 and -17.4 mV was obtained for spherical nanoparticles and nanospindles of silica respectively. The above studies suggest that the particles are well capped by the cationic surfactant. These surfactants have a positive charge on their head group which helps in formation of an assembly of surfactant molecules on the surface of nickel oxalate nanorods.

Fig. 2—Nickel oxalate nanostructures synthesized using (a) CTAB/1-butanol/n-hexane, (b) Tergitol/1-octanol/cyclohexane and (c) TX-100/1-hexanol/cyclohexane. Copper oxalate nanostructures synthesized using (d) CTAB/1-butanol/cyclohexane, (e) Tergitol/1-butanol/cyclohexane and (f) TX-100/1-butanol/cyclohexane. Silica nanostructures synthesized using (g) CTAB/1-butanol/iso-octane and (h) Tergitol/1-octanol/cyclohexane.
the growing nanorods (bearing negative charge). It is probable that there is no association of surfactant molecules (CTAB) on the initial nuclei in the water-rich domains (Fig. 1) whereas the non-ionic surfactants like TX-100 and Tergitol associate on all the domains both on the water-rich and on those having no water on the sides. This results in uniform growth in all directions leading to spherical or cubic particles when the synthesis is carried out with neutral surfactant.

The other factors which affect the morphology and size of the product are the elastic constant of the surfactant film, intermicellar exchange rate, size, shape and charge of polar head group of surfactant and surfactant hydrophobic chain length.

The surfactant chain length also has an effect on the size and shape of copper oxalate nanoparticles which was studied using tetradecyltrimethylammonium bromide, TTAB (C-14) and CTAB(C-16) (Table 1, Fig. 1d). The length and diameter of the rods were found to decrease when the synthesis was carried out using TTAB. This is explained on the basis of higher packing efficiency and more rigid films for TTAB due to decrease in hydrophobic chain length. Polar head group of the surfactant also plays a significant role on the size and morphology of nanostructured materials. This was investigated on copper oxalate nanostructures which were studied by changing the polar head group to pyridinium from ammonium. A rigid surfactant layer is formed due to restricted orientation of pyridinium ion owing to its larger size. This leads to the formation of nanorods with low aspect ratio (1.5:1) (length, 750 nm and diameter, 500 nm) (Table 1, Fig. 1e).

Gao et al. have discussed the effect of the amount of surfactant (CTAB) on the formation of CuS nanowires and nanorods. Nanoparticles were formed when the synthesis was carried out in the absence of surfactant while with increase in the amount of surfactant the morphology of CuS changed from short nanowires, short nanorods to long nanowires. The change in morphology was explained on the basis of increase in the inter layer distance between two surfactant layers with increase in the amount of the surfactant. Chiang et al. synthesized cylinders, cubes and trigon of gold nanostructures using mixed reverse micelles formed using AOT and Span80 as the surfactants. Different morphologies of the nanostructures were obtained by the addition of NaCl solution to the reverse micellar system. The presence of chloride ions increased the nucleation rate and thereby affected the morphology.

### Role of Co-surfactant

The size and shape of ZnS nanoparticles was varied with variation in the chain length of co-surfactant along with $W_o$ by Charinpanitkul et al. Quintela showed that the surfactant film flexibility and coalescence rate increases on addition of co-surfactants and this result in the formation of larger sized particles.

Our group has studied the effect of co-surfactant by varying the chain length of the co-surfactants keeping the other parameters constant such as surfactant (CTAB). The co-surfactants used in our studies were 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol and 1-decanol. A change in the chain length of co-surfactant leads to variation in surfactant film flexibility which finally determines the growth of particles inside the reverse micelle. We observed an increase in the aspect ratio of copper oxalate rods with an increase in the carbon chain length of the co-surfactant from 1-butanol to 1-hexanol. This was attributed to decrease in the surfactant film rigidity with increasing chain length of co-surfactant leading to higher growth rate and an increase in the aspect ratio of copper oxalate sub-micron rods. The aspect ratio observed for these rods is summarized in Table 2. On further increasing the chain length of co-surfactant, 1-heptanol nanorods with a lower aspect ratio (6:1) were obtained when compared with 1-hexanol. The length and diameter of the nanorods formed with 1-hexanol is higher, though the overall aspect ratio is lesser. When 1-octanol was used as co-surfactant, nanocubes of

### Table 2—Copper oxalate nanostructures synthesized using microemulsions with different co-surfactants

<table>
<thead>
<tr>
<th>System</th>
<th>Co-surfactant</th>
<th>Copper oxalate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB/iso-octane/</td>
<td>1-Butanol</td>
<td>Nanorods</td>
</tr>
<tr>
<td>co-surfactant system</td>
<td></td>
<td>480 (l)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>130 (d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A R: 3.69:1</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>Nanorods</td>
<td>750 (l)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>175 (d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A R: 4.3:1</td>
</tr>
<tr>
<td>1-Hexanol</td>
<td>Nanorods</td>
<td>950 (l)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150 (d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A R: 6.33:1</td>
</tr>
<tr>
<td>1-Heptanol</td>
<td>Nanorods</td>
<td>1200 (l)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200 (d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A R: 6:1</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>Nanocubes</td>
<td>80-100</td>
</tr>
<tr>
<td>1-Decanol</td>
<td>Nanoparticles</td>
<td>8-10 (assembling to form nanorods)</td>
</tr>
</tbody>
</table>
size 80–100 nm were obtained, while nanoparticles of size ~8–10 nm were obtained with 1-decanol, which was attributed to a more rigid structure produced by the interaction of the alkyl chains of the co-surfactant with the surfactant tails. This results in reduced coalescence rate and hence particles of smaller dimensions were formed. This rationalizes the decrease in the size of nanostructures with an increase in the co-surfactant chain length beyond C₆ alcohols.

**Role of Water Content (WO)**

Structural diversity in the product can be also achieved by varying the water-surfactant molar ratio. Such a study was carried out by Lai et al.²⁸ where the morphology of calcium phosphate was varied from nanosphere, needle like, nanosheets and rod-like by varying the W₀ of the reverse micellar system from 5, 8, 10 and 15 respectively. Bagwe and Khilar⁸ in 1997 investigated the role of aqueous content on the size of AgCl nanoparticles. They observed an increase in particle size with W₀ of 5 to 10 whereas the size of particles decreased at W₀ of 15. Cason et al.⁷ observed an increase in the growth rate for copper nanoparticles with increasing W₀.

We have investigated the role of aqueous content²³ (W₀) of the system on the size and shape of the copper oxalate nanostructures synthesized using a neutral surfactant, Triton X-100. Here W₀ was varied (11, 14 and 16) while other parameters were kept constant. We observed an increase in the size of nanocubes with increase in W₀ (Table 3) which was explained on the basis of higher intermicellar exchange rate due to increase in flexibility of the surfactant film. With the increase in the intermicellar exchange rate, an increase in the size was observed.

**Other Parameters**

The ligand attached to the transition metal ions influences the morphology of the product. This is illustrated by taking copper oxalate and copper succinate²⁹ as example where copper in one case is bound to oxalate ion, while in the other it is bound to succinate ion. Succinate ion differs from oxalate group by having two methylene groups between the carboxylate ions whereby a 7-membered ring structure was proposed for the copper succinate dihydrate in an octahedral environment. This differs from copper oxalate where the oxalate ion forms a five-membered ring with Cu ion in square planar arrangement. Thus, the incorporation of two methylene groups introduces strain in the microstructure, resulting in variation in the size, texture and microstructure of copper succinate dihydrate.

The role of molar ratio of the reactants also plays a critical role in the morphology of the product as also observed from the studies carried out by Xu et al.³⁰ The authors have shown that variation in the molar ratio of I⁻:Ag⁺ leads to formation of nanoparticles and nanowires of AgI. Higher molar ratio (2 or 3) was preferred for the formation of nanowires while a molar ratio of 1 was preferred for the formation of nanoparticles. The authors have attributed this to the formation of silver-iodide complex such as AgI₂, AgI₃²⁻, etc. which may decrease the growth of formation of nuclei resulting in the formation of one-dimensional structures.

**Conclusions**

Microemulsions can be used to design a large number of nanostructures. Proper choice of the parameters involved in the formation of microemulsions, viz., the nature of surfactant, co-surfactant, solvent and the amount of aqueous content can help in controlling the size and shape of the nanostructures. Our studies show that cationic surfactants help in the formation of rod-like morphology for particles bearing a negative surface charge whereas spherical or cube-shaped nanostructures were obtained by using non-ionic surfactants. We believe that the review will give a better understanding to those working in the field of synthesizing anisotropic nanostructures for their potential applications. This method is a very versatile method and can be utilized for the controlled synthesis of variety of nanostructured materials with varied shape and size. We believe that the understanding of the role of various parameters involved in the synthesis of nanostructured materials using microemulsions will benefit researchers working in the area of nanoscience and nanotechnology. However, this field can further have wider applications if biosurfactants are used for the formation of microemulsions.

<table>
<thead>
<tr>
<th>System</th>
<th>W₀</th>
<th>Shape</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triton X-100/cyclohexane/1-hexanol system</td>
<td>11</td>
<td>Nanocubes</td>
<td>35-50</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>Nanocubes</td>
<td>50-60</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>Nanocubes</td>
<td>80-100</td>
</tr>
</tbody>
</table>

Table 3—Copper oxalate nanostructures synthesized using microemulsions with different W₀.
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