Mechanistic Investigations of Growth of Anisotropic Nanostructures in Reverse Micelles

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1. INTRODUCTION

The size and shape of nanostructures govern the unique properties of nanoparticles. Among the various shapes, anisotropic nanostructures have shown enormous potential in diverse applications and, hence, immense efforts and resources have been deployed on strategies for fabricating such 1D nanostructures with controlled size, aspect ratio, and monodispersity.1−10 Anisotropic particles exhibit direction- and dimension-dependent physical and chemical properties. Particle anisotropy results in features and functions that are not possible simply by size-tuning of spherical nanoparticles. A minor change in the aspect ratio may result in a much better control of tunability of the properties than obtained by changing the size of the nanoparticle. For example, while it is possible to tune the optical properties of anisotropic silver or gold nanorods throughout the visible, near-infrared, and infrared regions by variation of the aspect ratio, it is not possible to tune the optical properties of anisotropic silver or gold nanospheres. A minor change in the aspect ratio may result in a much better control of tunability of the properties than obtained by changing the size of the nanoparticle. For example, while it is possible to tune the optical properties of anisotropic silver or gold nanorods throughout the visible, near-infrared, and infrared regions by variation of the aspect ratio, it is not possible to tune the optical properties of anisotropic silver or gold nanospheres.

14 Anisotropic Mn-Zn ferrite nanoparticles increased the blood circulation time as compared to isotropic ones and thus were potentially more useful in biomedical applications.15 One reason for this is perhaps that these structures of well-controlled size and shape possess specific crystallographic facets, which are prominent. For example, it was seen that La$_2$NiO$_4$ nanorods are selectively terminated by NiO moieties as opposed to nanospheres of the same composition and phase that are terminated by LaO moieties.16 This leads to the nanorods of La$_2$NiO$_4$ being an order of magnitude more efficient in surface oxygen exchange activity than the nanospheres.

Anisotropic nanostructures have been synthesized with numerous well-established and documented chemical and physical preparation methods such as chemical vapor deposition, hydrothermal/solvothermal, vapor-liquid-solid (VLS), co-precipitation, sol-gel, wet chemical synthesis by substantially in anisotropic particles as compared to isotropic ones.14 Anisotropic Mn-Zn ferrite nanoparticles increased the blood circulation time as compared to isotropic ones and thus were potentially more useful in biomedical applications.15 One reason for this is perhaps that these structures of well-controlled size and shape possess specific crystallographic facets, which are prominent. For example, it was seen that La$_2$NiO$_4$ nanorods are selectively terminated by NiO moieties as opposed to nanospheres of the same composition and phase that are terminated by LaO moieties.16 This leads to the nanorods of La$_2$NiO$_4$ being an order of magnitude more efficient in surface oxygen exchange activity than the nanospheres.
thermodynamic stability of supramolecular self-assemblies consisting of nanosized water droplets (polar liquid) dispersed in a continuous nonpolar oil phase stabilized by surfactants and, in some cases, also by cosurfactants at the water/oil interface. The most striking feature of MEDs is that the nanometer-sized aqueous core acts as nanoreactors within which controlled reactions lead to the formation of a wide array of nanostructures with a relatively narrow size distribution. In addition to acting as nanoreactors, these MEDs also exhibit the unique property of being able to control the homogeneity and monodispersity because the surfactants can adsorb on the particle surface once the sizes of water pool and encapsulated nanoparticles become comparable. Thus, the RM prevents the process of aggregation of nanoparticles and hence are widely known as the shaping vesicles for inorganic nanostructures. The RMs have been broadly divided on the basis of the presence (or absence) of cosurfactant at the interface (water/oil) as (1) ternary RMs (surfactant/oil/water) and (2) quaternary RMs (surfactant/cosurfactants/oil/water). Compared to the ternary systems, the quaternary systems are more complex, having a rich structural phase diagram with a wide number of possible structural geometries such as spheres, ellipsoids, cylinders, and sponge-like as well as lamellar structures. The possibility of achieving such a wide variety of structures is the very essence of RMs facilitating other applications, e.g., extraction of proteins apart from the synthesis of nanoparticles. Owing to a variety of micellar architectures, the quaternary RMs as nanoreactors have led to novel anisotropic nanostructures and hence have been recognized to have many advantages over conventional ternary RMs. For example, in comparison with the anionic (bis(2-ethylhexyl)sulfosuccinate, AOT) ternary reverse micelle system, the droplet size of the quaternary cationic (cetyltrimethylammonium bromide, CTAB) reverse micelles can be more precisely tuned by varying the cosurfactant values with additional modulation due to the presence of cosurfactants at the interface (water/oil). Our group has utilized the quaternary RMs as a soft template and successfully synthesized a variety of nanoparticles possessing different geometries over a relatively narrow size distribution, homogeneity, and monodispersity.

2.2. Synthesis of Nanoparticles in Reverse Micelles. RMs have been widely accepted as ideal templates for the synthesis of a variety of nanostructures. The key advantage is the ability to obtain size control by a relatively inexpensive method where there is no requirement of expensive and sophisticated instruments used in several other physical synthesis methods such as plasma synthesis, flame spray pyrolysis, chemical vapor deposition, laser evaporation, etc. Additionally, this method has a number of advantages such as (1) the spontaneous formation of the well-separated domains in MEDs, (2) the presence of monodispersed droplets, which act as confined and tunable nanoreactors, and (3) a microhomogeneous product with the desired stoichiometry preserved inside the aqueous core and a remarkable ability to fine-tune the nanoparticle’s structural characteristics (size, shape, and morphology). In addition, this method is highly tunable due to the modulation of parameters influencing (1) the interfacial film rigidity of MEDs and (2) kinetics of crystal growth in a confined environment. The interfacial film flexibility of MEDs can be affected by modulating the following parameters: (1) water-to-surfactant molar ratio \( W_0 \), (2) structure of the surfactant and...
cosurfactant,\(^{21,23,60}\) (3) nature of the continuous organic solvent,\(^{21−23,60}\) (4) intermicellar exchange rate,\(^{54}\) and (5) packing parameter.\(^{19}\)

In 1982, RM technique was utilized for the first time to synthesize metal nanoparticles of Pt, Rh, Pd, and Ir by Boutonnet et al.\(^{61}\) Since then, a great variety of inorganic nanoparticles have been synthesized using the MED approach that includes simple metal nanoparticles (Ag, Pt, Rh, and Pd),\(^{52−64}\) metal oxides (Fe\(_2\)O\(_3\), ZrO\(_2\), TiO\(_2\), and CeO\(_2\) ),\(^{65−68}\) doped and mixed metal oxides (Ce\(_{0.99}\)Eu\(_{0.01}\)O\(_2\), Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\), and Zr\(_{0.99}\)Eu\(_{0.01}\)O\(_2\) ),\(^{69,70}\) metal chalcogenides (Ag\(_2\)S, Ag\(_2\)Se, ZnS, PbS, CdS, and CdSe),\(^{71−75}\) phosphates (Ca\(_3\)(PO\(_4\))\(_2\) and CePO\(_4\) ),\(^{78,79}\) and fluorides (PrF\(_3\), YF\(_3\), CaF\(_2\), and NdF\(_3\) ).\(^{33,80−82}\) Our group has been extensively involved in microemulsion-based nanoparticle synthesis and also in understanding the role of various physiochemical parameters of these emulsions to tailor the nanostructure size and shape.\(^{21,22,30,88,89}\) In our earlier reports, we have reported insights into the specific role of CTAB surfactants in the RM-based formation of elongated nanorods.\(^{83,84}\)

### 2.3. Dynamics of Reverse Micelles

MEDs have been utilized as chemical reactors because of their unique interfacial properties, which facilitate a close contact of hydrophilic and hydrophobic domains at the nanoscale level.\(^{37,38}\) One of the most important attributes of these MEDs is their dynamic nature and, therefore, they are regarded as the soft templates. In addition, owing to the rich phase diagram, these MEDs can acquire a variety of structures to aid in the growth of nanostructures within their core.\(^{32,37,38}\) The evolution of the nanostructures within the confined environment of a reverse micellar self-assembly is a heterogeneous growth process involving a variety of intermediate entities.\(^{85,86}\) Because of the Brownian motion, the nanometer-sized MEDs undergo continuous collisions and form an encounter pair (or a fused dimer), which results in the interchange of reactants with a rate constant of \(k_{\text{ex}}\) (Figure 1A).\(^{21}\) The interdroplet exchange is an important step and its characteristic timescale lies in the range of \(10 \mu s < \tau_{\text{ex}} < 1 \text{ ms}\). It is known that several MEDs (some studies suggest up to 6) may be interacting. A timescale analysis has been reported for the precipitation of CaCO\(_3\) in a typical microemulsion system: the chemical reaction \(\tau_{\text{chem}}\) (10\(^{-12}\) to 10\(^{-8}\) s), the nucleation \(\tau_{\text{nuc}}\) (10\(^{-12}\) to 10\(^{-8}\) s), the intermicellar exchange \(\tau_{\text{ex}}\) (10\(^{-8}\) to 10\(^{-3}\) s), and the particle growth \(\tau_{\text{g}}\) (10\(^{-3}\) to 10\(^{-1}\) s).\(^{85}\) It has been explicitly shown that both the chemical reaction and nucleation are very fast with respect to the lifetime of the transient dimer.\(^{85}\) Therefore, once the dimer is formed, the exchange of reactants occurs through the nanochannels and nucleation starts instantly at the micellar edges following the known growth model—from the boundary to the core.\(^{19,86}\) Every droplet collision does not result in dimer formation. This is determined by the encounter rate factor, \(\gamma\), which depends on film flexibility.\(^{21,87}\) A number of other factors govern the fusion—fission process of the microemulsion system such as the volume fraction \(\phi\), the MED size, \(W_0\) (water-to-surfactant molar ratio), concentration of reactants, temperature, critical nucleus \(n^*\), etc.\(^{21,22,30,88,89}\) Figure 1B depicts a single RM system, where one of the reagents is added as an ME and the other is present in solution form.

### 3. TECHNIQUES TO INVESTIGATE MECHANISMS OF INTERACTION OF MEDS

The primary instrumental techniques that have been discussed in this paper for investigation of mechanistic aspects of synthesis of anisotropic nanostructures in MEDs through the RM method are discussed. Just the basic concepts are provided and, for a detailed description of the techniques, the reader is referred to appropriate sources mentioned in references. Table 1 summarizes the techniques and lists the relevant equations used in the analysis of data obtained from the respective instrumental technique.

#### 3.1. Dynamic Light Scattering (DLS).

DLS is one of the most common tools for the characterization of reverse micelles due to its relatively low cost and ease of use. This technique is used for the determination of nanoparticle size in colloidal suspensions along with the polydispersity index of the sample and stability of formulations. This technique also allows us to detect the presence of agglomeration or aggregation of
### Table 1. Summary of Instrumental Techniques Used to Investigate Mechanistic Aspects of RM Systems

| technique           | principle                                                                 | information obtained                                                                 | relevant equations                                                                 | notation |
|---------------------|---------------------------------------------------------------------------|--------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|----------|
| DLS<sup>44,50</sup> | light scattering                                                          | (1) NP size in colloidal solutions                                                  | $D = \frac{1}{2D_{\parallel}}$ (1)                                               | k = Boltzmann constant; $T = $ temperature; $\eta = $ viscosity of solvent; $D =$ diffusion coefficient parallel to the major axis ($D_{\parallel}$) and minor axis ($D_{\perp}$) and total $D$ |
|                     | (2) polydispersity index                                                  | $D_{\parallel} = \frac{54}{20\pi^2} \ln \left( \frac{1}{\lambda} \right)$ (2)     |                                                                                  |          |
|                     | (3) stability of colloidal suspension                                     | $D_{\perp} = \frac{54}{20\pi^2} \ln \left( \frac{1}{\lambda} \right)$ (3)        |                                                                                  |          |
|                     | (4) presence of aggregation or agglomeration                              | $D_T = (D_{\parallel} + 2D_{\perp})/3$ (4)                                         |                                                                                  |          |
|                     | (5) diffusion coefficient (with knowledge of viscosity of solution)       |                                                                                      |                                                                                  |          |
| SAXS<sup>91</sup>   | scattering of X-rays detected at small angles                             | (1) size                                                                               | $q = \frac{2\pi}{\lambda} \sin(\alpha)$ (5)                                   | $q =$ length of scattering vector or momentum transfer; $\alpha =$ scattering angle; $K =$ contrast; $\lambda =$ incident beam; $\lambda (\text{s})$; and matrix ($\text{s}$); $P(q) =$ form factor; $S(q) =$ structure factor |
|                     | (2) structure of MED                                                      | $I_{\text{saxs}} - I_{\text{sample}} = K_{\text{SP}} P(q) S(q)$ (6)                  |                                                                                  |          |
| TCSPC<sup>92</sup>  | detection of single photons emitted by a sample with precise record of its arrival time w.r.t. a reference signal, which is of the corresponding excitation pulse | (1) lifetime of fluorophore                                                           | $P(t) = \sum_{n=0}^{\infty} \alpha_n \exp(-\gamma t)$ (7)                     | $F(t) =$ fluorescence decay; $\alpha_n =$ amplitude of fluorophore; $\gamma =$ lifetime of fluorophore; $\gamma (0); v (\text{s})$ and $e(\text{s})$ presenting the peak frequencies at time $t, 0$, and $\infty$ respectively; $I_P$ and $I_I$ refer to the vertical and horizontal polarized components of the emission intensity, respectively; $G$ is the correction factor |
| FCS<sup>92</sup>     | fluctuation of fluorescence intensity due to diffusion of a fluorophore in a small (approximately nanoliter) observed volume | (1) diffusion coefficients                                                             | $G(r) = G(0) \left( 1 + \frac{r}{\eta} \right)^{-1/2} t^{-1}$ (10)             | $G(0) = 1/N; \eta =$ diffusion time (related to the MW) of the fluorophore; $s =$ radius; $u =$ half-length (see figure 3) |
|                     | (2) hydrodynamic radii                                                    |                                                                                      |                                                                                  |          |
|                     | (3) average concentrations                                                |                                                                                      |                                                                                  |          |
|                     | (4) kinetic chemical reaction rates                                       |                                                                                      |                                                                                  |          |
|                     | (5) singlet-triplet dynamics                                              |                                                                                      |                                                                                  |          |
| EXAFS<sup>93</sup>  | scattering of the photoelectrons ejected from the absorbing atom         | (1) coordination number                                                                | $x_i(k) = \frac{2k}{zz_{\parallel}(k)} \ln \left[ 2\Re R_i - \frac{k^2}{2} + \delta(k) \right] e^{-2\pi^2 R_i}$ (11) | $x(k) =$ absorption coefficient of one atom; $k =$ photoelectron wavenumber; $zz_{\parallel}(k) =$ photoelectron scattering-path amplitude and phase; $z_\parallel =$ passive electron reduction factor; $n_i =$ degeneracy of the scattering path; $R_i =$ effective half-path length; $\sigma_i^2 =$ mean-square deviation in $R_i$; $\sigma_i^2 =$ third cumulant of the radial distribution function; $x_i(k) =$ photoelectron mean free path; $n_i =$ coordination number of the $i$th shell at the radius $R_i$; $2N_{A/l}(i) =$ total number of the nearest $A$–$A$ (same type) neighboring atoms within the same coordination shell; $N_A =$ total number of similar type (A) of atoms in the cluster |
|                     | (2) distance from the selected atom to neighboring atoms                  |                                                                                      |                                                                                  |          |
|                     | (3) structure of neighboring atoms                                        |                                                                                      |                                                                                  |          |
|                     | (4) degree of disorder                                                    |                                                                                      |                                                                                  |          |
| XANES<sup>93</sup>  | scattering of the photoelectrons ejected from the absorbing atom         | (1) electronic structure of unoccupied levels                                          | $S(T, P) = \frac{A}{\alpha(\text{P}) - \epsilon - \epsilon_1} + BT + C(P)$ (13) | $A_{\text{metal} - \text{adsorbate}} =$ metal–adsorbate interactions via the $(P, T)$-dependent adsorbate coverage; $BT =$ contribution from the metal–support interaction; $C(P) =$ contribution from the adsorbate–support interaction |
|                     | (2) oxidation state of elements                                           |                                                                                      |                                                                                  |          |
|                     | (3) adsorbate–support, particle–adsorbate, and particle–support interactions |                                                                                      |                                                                                  |          |
| NMR                 | loss of degeneracy of nuclear spin energy levels on application of an external field | (1) molecular composition                                                             | $\mu_i = \gamma B L_i$ (14)                                                     | $\mu_i =$ component of the nuclear magnetic moment along the $z$ axis; $\gamma =$ magnetogyric ratio; $h =$ Plank's constant; $\gamma B =$ energy corresponding to the nuclear spin orientation; $\mu_i =$ Larmor frequency; $B =$ applied magnetic field |
|                     | (2) connectivity                                                          |                                                                                      |                                                                                  |          |
|                     | (3) neighboring groups, either                                            |                                                                                      |                                                                                  |          |
the nanostructures. It measures the hydrodynamic size of particles based on the principle of scattering of light from a laser, which passes through a colloidal solution, and analyzes the modulation of the intensity of scattered light as a function of time. It is based on the assumption that particles are spherically shaped. Hydrodynamic radii of the particles are correlated to the Brownian motion of the particles. The smaller the particle size, the more readily it will diffuse than the larger particles, and the DLS instrument will generate a correlation function between the particle size and its time-dependent light scattering capacity. For spherical particles, the obtained DLS data after coupling with the known information of solution viscosity helps in finding out the diffusion coefficient for the particles using the Stokes–Einstein equation (eq 1, Table 1).

For asymmetric particles, eqs 2–4 (Table 1) may be used. Thus, asymmetry of MED can also be predicted.

3.2. Small-Angle X-ray Scattering (SAXS) 91

SAXS gives information about the size and structure of MEDs. A collimated X-ray beam irradiates a sample at low angles between 0.02° and 10°. The detector detects an interference pattern resulting from the scattered radiation falling on it after interaction with the sample. Depending on the angle of observation 2θ, orientation, and distance (r) between the atoms interacting with the radiation and the detector, this pattern may be a result of constructive or destructive interference and gives us the information regarding the internal structure of the material. Scattering patterns are usually presented as functions of q known as "length of scattering vector" or "momentum transfer" (eq 5, Table 1). Experimentally, a scattering curve is obtained by subtracting the intensity of sample I_{sample} from that of the matrix material (Figure 2a) and may be mathematically represented as eq 6 (Table 1).

A double-logarithm curve (Figure 2b) yields information about the structure. At small angles, the slope of form factor gives the overall size, while at large angles, surface-related information is obtained. The middle section of the form factor gives information related to the shape and the internal density distribution. In this region, a slope of 0, −1, or −2 in a double logarithm indicates a globular, cylindrical, or lamellar shape, respectively. The oscillating part of the form factor can be effectively investigated by transforming it into real space via Fourier transformation that yields the pair-distance distribution function (PDDF), which in turn yields information about the shape of the particle (Figure 2c).

3.3. Time-Resolved Fluorescence Spectroscopy 92

Time-resolved measurements appreciably add to our understanding of the kinetics of inter- and intramolecular processes of chemical systems under investigation. Time-resolved measurements may be performed in the time domain or in the frequency domain. In time-domain measurements, a pulse of light, ideally considerably shorter than the decay time, τ, of the fluorescent sample under investigation, is employed for the excitation of a fluorescent sample (Figure 3). The expression of fluorescence lifetime decay I(t) provides important insights into the reaction mechanism.
The obtained fluorescence decay data is then fit to an appropriate multi component exponential function. The lifetime and the corresponding amplitude are then derived from the fitting of the obtained fluorescence decay, \( F(t) \), to a sum of \( n \) exponentials as given by eq 7 (Table 1). Equations 8 and 9 (Table 1) are the other relevant equations used to process the data.

### 3.6. Fluorescence Correlation Spectroscopy (FCS)\(^9\)

In FCS, temporary, time-dependent, and characteristic fluctuations of the fluorescence intensity due to freely diffusing fluorophores or molecules in and out of a small observed volume, \( V_{\text{eff}} \), are measured (Figure 4). Usually, \( V_{\text{eff}} \) depends on the shape of the detection function; for an ellipsoid, the value of \( V_{\text{eff}} \) is 0.35 fl. When a single fluorophore molecule diffuses into this volume, it can get excited and emit photon energy as fluorescence. Provided that the number of fluorophores is reasonably low (dilute solutions), monitoring the fluctuations in the fluorescence intensity in the specified volume yields information about their number, diffusion parameters, and dynamics in the observed volume. Steady-state FCS describes the luminescence properties and time-resolved FCS demonstrates the lifetime of the excited states. The random diffusion of the number of fluorophores in a specified volume can be determined by the Poisson statistics. The time-dependent fluorescence intensity is studied mathematically to describe the frequency and amplitude distribution of fluctuations. A fluorescence correlation emission spectrum is a plot of the amplitude \( G \) as a function of time \( \tau \). Primarily, FCS deals with the measurement of translational diffusion, which depends on the size of the fluorophores and their interaction with other fluorophores. The autocorrelation function for the three-dimensional diffusion of an ellipsoid observed volume is represented by eq 10 (Table 1).

### 3.7. X-ray Absorption Spectroscopy (XAS)\(^9\)

X-ray absorption spectroscopy (XAS) uses the tunable and intense X-rays generated in a synchrotron that penetrate liquids and thus are informative probes for monitoring the in situ growth of MED and the nanostructures that grow inside them. The photon energy is tuned in the 0.1–100 keV region, where core electrons can be excited. The edges are named after the identity of the excited core electron, with K, L, and M corresponding to whether the core electron is excited from principal quantum number \( n = 1, 2, \) or 3, respectively (Figure 5).
Spectroscopic and X-ray di
nanoparticle as opposed to some other methods like
advantage of TEM data is that it provides a direct image of a
to monitor the growth of
interior of nanoparticles, for example,
surface areas, showing arrangement of atoms and,
detailed images of the interior of nanoparticles, for example,
instruments can provide atomic-level resolution of the
interior of nanotubes. However, the use of transmission
electron microscopy (TEM) especially high-resolution TEM
instruments are restricted by expensive instrumentation and
Cu grids used to deposit samples.

3.9. Nuclear Magnetic Resonance (NMR). Several nuclei possess spin angular momentum. Any nucleus that has
an integer or half-integer spin quantum number, I, has a
component of angular momentum \(m_I\) around an arbitrary axis
where \(m = I = I - 1, I - 2, \ldots, -I\). For nuclei with \(I > 0\), each
value of \(m_i\) corresponds to a different orientation of nuclear
spin and, thus, a different nuclear magnetic moment. The
component of the nuclear magnetic moment along the z-axis,
\(\mu_z\) is proportional to the component of spin angular
momentum along that axis (eq 14, Table 1 ) with the
coefficient of proportionality being \(\gamma\), the gyromagnetic ratio.
On application of an external magnetic field, \(B_0\) the different
\((2I + 1)\) orientations associated with different energies (eq 15,
Table 1 ) lose their degeneracy. These energies are often
expressed in terms of the Larmor frequency (\(\nu_0\), eqs 16 and 17,
Table 1 ). For nuclei with \(I = 1/2\), the possible values of \(m_1\) are
+1/2 and \(-1/2\) denoted as the \(\alpha\) and \(\beta\) states, respectively,
with an energy separation of \(h\nu_0\). When \(\gamma\) is positive (as for most nuclei), the \(\beta\) state lies above the \(\alpha\) state and the
population of spins in the latter is slightly higher than in the
former (Figure 6). On application of an external radiation of
frequency \(\nu\) such that \(\nu = \nu_0\), the energy separations come into
resonance. Under this condition, the nuclear spins and the
radiation of frequency $\nu$ are coupled strongly and the spins make a transition from the $\alpha$ state to the $\beta$ state. NMR is a technique used to investigate the composition, structure, reaction kinetics, and other properties of molecules containing magnetic active nuclei. A magnetic field is applied that induces a separation of energy levels corresponding to the different orientations of the nucleus. The frequency at which the separated energy levels come into resonance with an oscillating electromagnetic field is observed. The nuclear magnetic moment interaction with moments of neighboring magnetic nuclei influences this resonance frequency and yields important information about the chemical environment of the nucleus under study. A higher magnitude of the magnetic field results in a higher population difference between the different states and energies as well as a greater energy of each absorbed photon. There are numerous examples in the literature on the application of NMR spectroscopy for investigation of RM assemblies.96 Usually, the changes in the environment of the moieties containing organic groups like the surfactant and cosurfactant are monitored and, as we shall see below, these changes provide valuable mechanistic information.

4. CASE STUDIES

4.1. Mechanism of Growth of Metal Oxalate Nanoparticles. 4.1.1. Monitoring the Size and Morphology of MED and Nanoparticles Growing inside Them. Metal oxalates are an important class of compounds as these are precursors to the corresponding metal oxides. Traditionally, oxide compounds are synthesized by high-temperature methods that do not allow control over their size and morphology, characteristics that can have a profound effect on various properties (e.g., catalytic properties) of these oxides. Thus, an in-depth knowledge of the mechanistic aspects of the nanostructure formation in MED systems would enable us to tailor the synthesis to obtain the desired size and morphology of these oxalates and, thus, the corresponding oxides.

Our group has previously studied the detailed mechanistic aspects of the growth of nanostructures in reverse micellar systems and we reported the first extensive study to explain the kinetics of MED interactions.83 Primarily, FCS, complemented by DLS and TEM, was employed to investigate the slow kinetics of the growth mechanism of iron oxalate ($FeO_x$) nanorods in the MEDs of the cetyltrimethylammonium bromide (CTAB)/1-butanol/isooctane MED system. The reaction was monitored for 8 successive days. Using FCS, the growth and reaction kinetics of MED-encapsulated FeO$_x$ nanostructures in a small volume ($\sim 1$ fL) of water-in-oil MEDs were monitored by correlating fluctuations in the fluorescence intensity from the probe dye sulforhodamine-B (SRh-B) encapsulated in the MEDs. In solution, MEDs during the course of their random motion can come close to each other to form “encounter complexes”, which form and separate at very high rates. A very few droplets (1 in $\sim 5000$) coalesce to form a “transient dimer”. FCS allows observation of the formation of the transient dimer but not the encounter complex due to time resolution limitations. The transient dimer allows intermicellar exchange of both the reactants and the dye. The former may lead to the formation of products, while the latter leads to fluctuations in fluorescence intensity, which are the basis of FCS measurements.

In each of the 8 days (total period under study), on observing the normalized FCS curves (Figure 7a), we see a
which de- 

data (Figure 7b), the following key inferences were drawn: (1) from day 6 onward. Overall, using the FCS, TEM, and DLS trend as the rate. Correspondingly, TEM nanorods were seen much faster than 

dominated growth period of 

declined slightly followed by a signi-

dividual MEDs that lead to formation and decomposition, respectively, of a transient dimer. Higher timescales (>~150 μs) correspond exclusively to the diffusion of the droplets. The timescale for the triplet conversion of the dye is of the order of 1 μs, which is much faster than τex and can thus be neglected. Analysis of the FCS data with a suitable kinetic model yielded the dimer lifetime (τex) and association rates for each day. It was seen that τex remained constant (~28 μs) for each day throughout the entire 8 day monitoring period. Until day 2, the rate of association of the coalescence of the droplets decreased slightly followed by a significant increase until day 6 (maximum value kassoc = 3.55 × 10^4 s^-1) and a subsequent decrease during days 7 and 8. The equilibrium constant K, which defines the tendency of droplet fusion, displays the same trend as the rate. Correspondingly, TEM nanorods were seen from day 6 onward. Overall, using the FCS, TEM, and DLS data (Figure 7b), the following key inferences were drawn: (1) There is a long nucleation-dominant growth period of ~3~4 days where the MEDs and, consequently, the nanostructures within them grow to a critical size of ~53 nm. (2) This was followed by a short period (days 4 and 5) where isotropic nanoparticles switch over to anisotropic growth to form nanorods and, (3) thereafter, a third period is where the nanorods grow in length by droplet association (Figure 7c).

Another key inference was that the droplet association rate correlates with the nanoparticle growth mechanism. The oxalate rods are decomposed to yield iron oxide nanoparticles. The composition of these oxide particles was found to depend on the decomposition conditions.65 On decomposition at 500 °C in air, spherical α-Fe2O3 NPs (~50 nm) were obtained, while cuboidal Fe3O4 NPs were obtained on decomposition at 500 °C in a vacuum of 10^-5 torr. The magnetic properties of the iron oxide nanorods were dependent on their phase and size.

Continuing our work on oxalate nanostructures, we carried out a detailed mechanistic study on the anisotropic growth of zinc oxalate (ZnOx) nanostructures within CTAB/1-butanol/isooctane MED systems.7 The difference of the ZnOx system with the FeOx system is that the kinetics are much faster and, thus, the reaction was monitored for 15 h for the former as compared to 8 days for the latter. On faster timescales, analogous to the FeOx system, in the ZnOx system too, by using a combination of SAXS, DLS, and TEM, the generation of nuclei, their aggregation to a critical size, and thereafter, the growth of anisotropic nanostructures of higher dimensions in the as-formed self-assembled MED templates were observed. However, all mechanistic aspects were not similar as we shall see below.

The primary aim of this study was to correlate the size and shape of the perturbed MEDs with the resulting nanostructures and get insights into the mechanisms of the reaction. As discussed above, SAXS studies allow us to observe the shape and size of the MEDs. Two types of MEDs and their aggregates were seen by SAXS and confirmed by DLS analysis. One type of MED was smaller in size (~4 nm) and spherical in shape. The second type of MED was larger and anisotropic and it was the site of reaction and growth of the nanostructures. Figure 8a presents the SAXS data that tracks the growth of these larger MEDs, while Figure 8b tracks the growth of all the MEDs present in the reaction mixture. It was seen (Figure 8b) that smaller and spherical MEDs (represented by d1) were present throughout the entire period of the reaction and were thus postulated to contain solubilized ions or by-products of the reactions. Monitoring the size and morphology of the larger MEDs (Figure 8a), it was seen that the bigger droplets...
or aggregates contain anisotropic ZnO nanostructures. Rod-like or cylindrical micelles were indicated by a pronounced peak on the lower-\(d\) (abscissa) side and an extended long tail on the higher-\(d\) side (Figure 8a). The peak \(d\) and the tail length correspond to the diameter and length of the rods, respectively. Overall, as indicated from the SAXS data (as magnified in the inset in Figure 8a), the peak \(d\) value increased and, simultaneously, the length of the tail also increased as the reaction proceeds. Thus, rod-like MEDs formed from cylindrical ones, which in turn formed from spherical ones. The aspect ratio was calculated from the \(d\) value and the length of the tail and further confirmed by DLS and TEM as appropriate.

Figure 8b tracks the change in particle size with time and Figure 8c depicts the proposed mechanism based on the consolidation results of all three experimental techniques. Spherical droplets were formed on mixing individual reactant MEDs. It is presumed that a transient dimer is formed analogous to the FeO\(_x\) case, but the short lifetime and size of this species hinder its detection by SAXS, DLS, or TEM. In the initial \(\sim 2\) h, the growth in size of the nanoparticles as determined by all the three techniques was the same. During this relatively short time, the spherical nature of the MEDs became ellipsoidal until they reached a critical size of 50–60 nm and an average aspect ratio of 4:1, indicating short nucleation-dominant particle growth. Thereafter, in the next \(\sim 2\) h, symmetry was broken and the formation of elongated nanoparticles with critical dimensions of 80 nm in length and 18 nm in diameter took place. After 4 h, due to its limited resolution, only smaller particles were observed by SAXS, while only nanorods were seen via DLS and TEM. Thus, these cylindrical structures with dimensions of 80 nm \(\times\) 18 nm self-assembled to form nanorods of very high aspect ratio (14:1 after 15 h) as seen by TEM. Additionally, this observation is corroborated by SAXS results, which showed that the rate of droplet coalescence reached its maximum after 4 h of reaction, indicating that the maximum rate of smaller droplets is fed into the lengthening nanorods.

Comparison of ZnO with FeO showed that the faster kinetics of nanorod formation directly correlate to the faster nucleation-dominant growth to reach a critical size, which immediately precedes the phase where the aspect ratio increased drastically and the nanorods grew in length. Thus, this period of nucleation-dominant growth was critical in governing the kinetics of metal oxalate nanorod formation. ZnO precursors obtained at different time periods as the reaction progressed were collected and decomposed to form ZnO and it was noticed that the morphologies of the oxide formed from precursors collected after about 1, 2, and 4 h and at longer durations were spherical (\(\sim 10–50\) nm), short nanorods (aspect ratio, 2:1), longer nanorods (aspect ratio, 4:1), and long nanorods of high aspect ratio, respectively. This indicated that the morphology of the oxalate precursors was retained in the oxides on decomposition. It may be mentioned that we have also reported the use of SAXS to investigate the mechanistic aspects of bare microemulsion systems. We have demonstrated that shape transitions can be directed in cationic (CTAB/hexanol/water/isooctane) MEDs from 1D cylindrical to prolate ellipsoidal by simply tuning the water-to-surfactant molar ratio during hydrotrope-induced structural growth in micellar droplets using SAXS.\(^{57}\) Hydrotrope is a salt (in this case, sodium salicylate) that modulates electrostatic interactions between the reverse micellar droplets and aids in the formation of self-assembled structures.\(^{98}\) In addition, we have also investigated the CTAB/\(n\)-hexanol/water/heptane reverse micellar system (at lower surfactant concentration) with the variation of hydrotrope concentration and water loading to manifest the 1D chain like assemblies of micellar droplets using SAXS.\(^{99}\)

The effect of the length of cosurfactant chain length on the growth kinetics (shape and size) of the MEDs formed as well as the shape and size of copper oxalate (CuO\(_x\)) nanostructures was investigated using SAXS.\(^{100}\) Two cosurfactants, 1-butanol (4 C) and 1-octanol (8 C), were used in the CTAB/cosurfactant/isooctane/water MED system. It may be mentioned here that the use of 1-butanol yields CuO\(_x\) nanorods, while 1-octanol yields CuO\(_x\) nanocubes. First, scattering data was obtained on bare MED systems (without metal ions) and, based on the variations in the electron density for the adjacent areas of the MEDs, the scattering data suggested a core–shell-like structure. When 1-butanol was used as a cosurfactant, the slope of the double-log plot was proportional to “1”, indicating the ellipsoidal/cylindrical-shaped MEDs, whereas when 1-octanol was used as a cosurfactant, the slope was proportional to “0”, indicating spherical MEDs. A negative deviation from Porod’s law indicated a gradual variation of the electron density between the two phases over a certain range of distance between them to form a diffused interfacial layer that corresponded to the surfactant (CTAB) molecules penetrating into isooctane. Previously, it was reported that alcohol cosurfactants with longer hydrocarbon chains favored the formation of MEDs as compared to the ones with shorter chains. The results of the model-free approach, namely, the variation in density, DL, and Porod plots, provided a guide for choice of model for fitting the SAXS data. Consequently, for 1-butanol and 1-octanol systems, ellipsoidal core–shell and spherical core–shell models were used respectively to fit the SAXS data and the average thickness of the diffused layer obtained by the model-independent method (Porod’s law) matched well with the thickness obtained using the models, thereby validating the choice of models.

For the case of ion-loaded MEDs using 1-butanol, the slope from the DL plot varied from 0.7 to 0.8, indicating the formation of ellipsoidal/cylindrical MEDs and CuO\(_x\) nanostructures. The development of CuO\(_x\) nanostructures was indicated by a positive deviation in the Porod plot that corresponds to the development of a sharp well-defined phase boundary. As the reaction progressed, the SAXS data of the reaction mix had to be fit to different models, spherical (0–20 min), ellipsoid core–shell/ellipsoid (40 min to 2 h), and ellipsoid core–shell/cylindrical (>2 h), providing insights into the progressive time-bound initiation of the reaction as well as change in shape, size, and/or anisotropy. The important features of this data beyond 1.5 h were (1) a sudden and extreme increase in the length of the cylindrical structure observed and (2) the growth exclusively along the length. The latter observation was postulated to support a previous observation that the surfactant molecules do not associate at the water-rich rod ends, thus facilitating an increase in the exchange of reactants with other micelles, leading to the growth along the length and the formation of rods. For the 1-octanol case, using an analogous approach, it was observed that the SAXS data could be fit to spherical shape (until 2 h) and spherical core–shell and sphere models (7–20 h). The initial observations in the model-independent analysis (DL, Porod’s law) were validated by the model-dependent approach.
Additionally, the volume of the spherical particle obtained on fitting of the average SAXS profile corresponded to the volume of a cube.

The differences in using the two cosurfactants arose from the film rigidity. This leads to the difference in kinetics as well as the difference in the shape of the MEDs and, thus, the obtained CuO$_x$ nanostructures. In the case of 1-butanol, the nucleation of the CuO$_x$ nanostructures occurred immediately after the start of the reaction, while for the 1-octanol case, separation of the CuO$_x$ nanostructures occurred after 7 h of the reaction. As mentioned earlier, the use of 1-butanol results in CuO$_x$ nanorods, while 1-octanol yields CuO$_x$ nanocubes. The SAXS results were further reinforced with TEM data.

**Scheme 1** presents a schematic of the proposed reaction.

Using Ni oxalate (NiO$_x$) as model nanostructures synthesized in the CTAB/1-butanol/isooctane MED system, the effect of the critical parameters $W_0$, solvent, and the surfactant identity on the size and morphology of the MEDs as well as the as-obtained nanostructures was investigated in detail. This reaction was also a “fast” reaction with a completion time of 15 h and FCS, SAXS, DLS, and TEM were used to monitor it. The reaction was carried out in three different surfactants, cationic CTAB, cetylpyridinium bromide (CPB), and nonionic TX-100, with other conditions remaining the same ($W_0=12$). When nonionic TX-100 was used, spherical NiO$_x$ nanoparticles with a size of approximately $\sim 30$ nm were obtained, while CTAB and CPB yielded nanorods. The rods obtained using CTAB had larger aspect ratios ($\sim 10:1$) than those obtained using CPB ($\sim 4:1$). Using CTAB, CPB, and TX-100, at the initial stages of the reaction, the sizes of bare MEDs respectively were around 4, 5, and 11 nm. The small size of the MEDs was postulated to be a mixture of reactants and nucleation-dominant nanoparticles. At the end of the reaction, these sizes are considerably larger; however, contrary to the initial stages of the reaction, in the nonionic surfactants, smaller MEDs and nanostructures were observed, as compared to those in cationic surfactants. This observation was rationalized in terms of interaction energy ($\gamma$) between water and the surfactant headgroup. The water–oil interfacial energy decreased appreciably on addition of surfactant molecules. The interfacial free energy $\Delta F = \Delta E - T\Delta S$, where $\Delta E$ and $\Delta S$ are the changes in interfacial energy and interfacial entropy, respectively, governs the stability of the MED system. Smaller MEDs are a result of stronger interaction ($-\gamma$) between water and the surfactant headgroup (as is the case for a cationic surfactant) that leads to a large water–oil interface. Among the cationic CPB and CTAB, the steric properties come into play and the former with a larger size headgroup that has less interaction with water results in larger MEDs than the latter.

After discussing the effect of the surfactant charge and the headgroup steric bulk on the size of the MED formed during the initial stages of the reaction, we discuss the effect of these factors as the reaction proceeds. It was previously discussed that cationic surfactants that contain positive headgroups form an assembly on the surface of growing metal oxalate nanoparticles due to negative $\xi$ potential (of the metal oxalate nanoparticles) and subsequently inhibit the MED (and, hence, the particle inside it) growth along the diameter of the nanoparticles, resulting in anisotropic micellar growth and, thus, the formation of nanorods. On the contrary, as seen experimentally too, nonionic surfactants (e.g., TX-100) result in isotropic structures. Another point to note is that in earlier discussions, where FeO$_x$ and ZnO$_x$ nanostructures were formed, using the MED method with CTAB as a surfactant, there was a critical size ($\sim 55$ nm) after which the shape and symmetry are switched to form anisotropic nanorods. Such a behavior was not observed when a nonionic surfactant is used.

After discussion on the effect of surfactant, we discuss the effect of variation in $W_0$, water-to-surfactant ratio, on the size and shape of the MED and, hence, the nanostructures formed inside them. It was seen that with the increase in $W_0$ both the bare MEDs and the ones containing growing nanostructures increase in size up to a certain $W_0$ (20 for bare MEDs and 16 for nanostructure-loaded MEDs) and then decrease. This was justified as follows. At a low value of $W_0$, the water content inside the micellar core is low. The limited water is constrained to hydrate a relatively large number of counter ions of the polar headgroup and the structure of water molecules modified into bound water. The paucity of water within the core made the micelle rigid. As the $W_0$ increased, the concentration of free water inside the water pool increased and this resulted in the micellar core being swollen, inducing the micellar growth. However, the finite bending modulus of the surfactant film that covers it, the MED, was prevented from growing indefinitely and, increasing the water content beyond a certain value, the
micellar core size decreased. It was postulated that two important parameters that play a crucial role in the formation and growth of particles, (1) the average ion occupancy number and (2) the intermicellar exchange, are affected by a change in $W_0$. These factors depend, among other variables, on the amount and type (bound or free) of water content and the bending modulus of the surfactant film. The DLS, TEM, and FCS studies clearly prove a linear relation between the size of reverse micellar templates and the nanostructures synthesized within them.

Now, we discuss the effect of the solvent chain length on the MED and nanostructures formed. The reactions were carried out using cyclohexane, $n$-hexane, and isooctane as solvents, maintaining the $W_0$ at 12 for all the cases. The droplet dimensions at the start of the reaction were approximately 3–4, 6–7, and 9–11 nm, respectively, for the case of isooctane, cyclohexane, and $n$-hexane; larger droplets/aggregates containing nanostructures were obtained after completion of the reaction ($15 \text{ h}$). However, the size of the nanostructures obtained followed a reverse trend, i.e., the smallest size of MEDs with nanostructures in the case of $n$-hexane and the largest in the case of isooctane. The entropy of mixing results in the penetration of shorter chain alkanes into the surfactant layers being effective than the longer chain homologues. The bulkiness of the solvent molecules leads to smaller reverse micelles, higher curvature, larger exchange rates, and larger dimensions of nanorods.

4.1.2. Investigation of Interior Domains of MED Using Solvation Dynamics. As we saw above, the mechanism of growth of anisotropic nanostructures inside MED assemblies has been investigated through complementary techniques like TEM, FCS, DLS, and SAXS. The reported studies remain limited to morphological aspects (size distribution and shape) of the perturbed MED system and missed important insights into alterations in MED’s interior domains during the heterogeneous growth process of nanostructures. Such information will essentially play a pivotal role in not only understanding the growth mechanism but also designing new potential synthetic schemes for the anisotropic nanostructures. Solvation is quite responsive to minor structural perturbations; therefore, it can provide valuable insights into perturbations in the MED’s interior en route nanostructure formation and hence stands to bring forward a mechanistic viewpoint. For solvation studies, the water molecules in the MED are observed. Essentially, the water molecules in the MED may be classified into three types depending on the environments they encounter: (i) free (bulk) water in the central core of the MED (these are the least perturbed water molecules and are far away from the interfacial region), (ii) the water trapped between the counter ions and surfactant polar headgroups (these are perturbed), and (iii) the bound water that resides in close proximity to the interface and have much retarded orientational relaxation. Previous studies have indicated that orientational dynamics exhibited by water molecules in the close vicinity of ions in solutions were substantially slower than bulk water. The surfactant–water phase interfacial layer played a key role in the formation of nanoparticles as the reaction and nucleation start at the micellar edges after the intermicellar exchange of reactants, with the subsequent growth occurring at this nucleation point. Mostly, noncovalent intermolecular interactions were present at the interfacial layer around the aqueous core resulting from the self-assembly of surfactant molecules. Thus, the soft template permits easy modification to induce the desired structural changes for the growth of nanoparticles, which are in turn reflected on the dynamics of water molecules.

In our recent work, solvation dynamics studies were used to probe different interior domains of MED systems that lead to the formation of nanorods. Two coumarin-based dyes, anionic C343 and neutral hydrophobic C153, were used to probe different regions of the MED systems. Extensive solvation dynamics experiments along with rotational relaxation studies were performed to monitor the growth of iron oxalate and zinc oxalate nanorods over 8 consecutive days and 15 h, respectively, inside the polar core of the CTAB/water/$n$-butanol/isoctane MED system. Additionally, the supernatant solution obtained after the extraction of nanostructures from the aqueous core was also examined to (1) investigate perturbed micellar aggregates and (2) see if the soft micellar templates carry an imprint of the rigid nanoparticles. Excited singlet-state decay and rotational anisotropy measurements were carried out using TCSPC instrument. For FeO$_n$ both the reaction mixture and supernatant were examined, while ZnO$_n$ due to the fast kinetics that lead to a turbid reaction mixture, only the supernatant was examined. The emission maxima exhibited a red shift for the Fe nitrate- and Zn nitrate-containing MEDs as compared to the bare and AmO$_n$ MEDs for both C343 and C153 dyes, indicating that the metal exhibited a polarizing effect on the dyes. However, due to the difference in polarity of the dyes, this shift was much lower in the latter than the former. The shift in Fe nitrate was more than Zn nitrate. For both C343 and C153, the emission maxima for FeO$_n$ MEDs exhibited a blue shift as compared to the metal nitrate peaks.

C343 is polar and was used to probe the polar regions of the MED core. The decays in the solvent correlation functions $C(t)$ in pure MEDs and AmO$_n$ were similar in the FeO$_n$ case and could be described as biexponential functions. The faster component was attributed to the free water molecules in the core of the MED, while the slower component could be attributed to the constrained water in the interfacial region. The decays in the Fe nitrate-containing MEDs and the FeO$_n$ MEDs had to be fit to a triexponential function, indicating alteration in water dynamics in the presence of metal. The third component is significantly slower than the remaining two. The magnitude of this rate-limiting component and, thus, the average solvation time increases until day 4 and subsequently drops. Interestingly, the $C(t)$ of the supernatant was also fit to a triexponential function and the solvation dynamics profiles of the aggregates in the supernatant and the MEDs with the loaded nanostructures match exactly (Figure 9). This strongly indicated that an imprint of the rigid nanostructures is left on the soft micellar templates. C153, a nonpolar dye, was used to get information on the nonpolar regions of the MED with the $C(t)$ exhibiting biexponential features. The trend exhibited by the decay parameters of the solvent correlation function was entirely different from the C343 case, indicating that the two dyes were probing different local environments. Due to the fast reaction rates and the resulting turbidity, TRES for ZnO$_n$ systems was carried out for the supernatant solution only and, similar to the FeO$_n$ systems, the decay of both C343 and C153 could be fit as triexponential and biexponential functions, respectively. For C343, showing analogous behavior as the FeO$_n$ system, the slowest component of the triexponential function increased (until about 6 h) and then decreased. Additionally, the TRES
The analysis indicated that for the ZnO case too, the nanostructures left lasting imprints on the soft micellar templates.

The rigidity or the viscosity of the surroundings strongly influences the rotational dynamics of the probe molecules and time-resolved anisotropy measurements were performed to investigate these aspects. For both the probe molecules C343 and C153, the rotation dynamics, \( r(t) \), function could be fit to biexponential functions, the faster component representing rotational dynamics of the bulk-like water (\( r_1 \)) in the micellar core and the slower one representing global rotational dynamics (\( r_2 \)) of the whole molecule. The probe C343 in the metal ion-containing MEDs exhibits a slower rotational time period than the pure and AmO\(_x\)-containing MEDs, indicating a distinct change in the surrounding rigidity in the presence of a metal. This was postulated to be a result of weaker interaction of NH\(_4^+\) with water as compared to the interaction of M\(^+\) with water. Among FeO\(_x\) and Fe nitrate, the former had slower rotational time. The trends in the slower time (global rotational dynamics) mirrored the trends in the C(t) for C343; it increased until day 4 and then decreased. The trends in \( r_2 \) was similar to both C153 and C343 for MEDs containing FeO\(_x\) nanoparticles. Additionally, the trend of \( r_2 \) was found to be similar for the case of surfactant aggregates (in the supernatant solution) and the nanoparticles for both probes C343 and C153, although the magnitude of the rotational time constant was slightly lower because of the absence of the nanostructures. In MEDs containing Zn nitrate and in micellar aggregates, the \( r_2 \) values of C343 and C153 were nearly invariant, irrespective of the reaction time.

In summary, the relaxation times provided the kinetic information about the three types of water environments present in the MED system. Additionally, the slowest time corresponded to the dynamics of the interfacial water that is most constrained. The kinetic analysis could be correlated to the nanoparticle growth dynamics.35,102 There is nucleation-directed growth, which led to nanostructures acquiring a critical dimension. Subsequently, these nanostructures acquiring a critical size switch their geometry from isotropic into anisotropic and the final step is elongation of the as-formed nanorods by coalescence.

4.2. Metal Oxide Nanoparticles. The synthesis of SiO\(_2\) by hydrolysis of TEOS catalyzed by ammonia 5-cyclohexane using a polyoxyethylene (S) nonylphenyl ethyl (NP-S)/cyclohexane/water ME was monitored by SAXS.\(^{103}\) The scattering data was modeled as a mixture of the silica particles and micelles. It is seen that the initial rate of growth of the silica particles was fast (Figure 10a), but subsequently, the reaction rate decreased and, at longer times, it was almost time-independent. In the same time frame, as seen from Figure 10b, the size of the reverse micelles decreased. The volume fraction versus time data for the growth of silica particles could be modeled with first-order kinetics w.r.t. TEOS concentration. However, the local volume fraction was two orders of magnitude larger than the expected SiO\(_2\) volume fraction and this was attributed to the “depletion interaction”. This phenomenon of an apparent high local density arises due to the exclusion of the smaller particles between the larger ones, leading to unbalanced osmotic pressure. For every mole of SiO\(_2\) produced from TEOS, 2 mol of water is consumed and 4 mol of ethanol is produced. The decrease in the size of the reverse micelles was attributed to this consumption of water. Repeating the SAXS measurement with added ethanol (equivalent to what would be produced in the reaction) in the MED system yielded similar-sized MEDs (as obtained in the original reaction), indicating that the majority of ethanol is expelled into the continuous organic phase. The number density of the particles remained constant after the first 10 h. At the beginning of the process, there was a strong variation in the number of particles due to the fast interdroplet exchange between the micelles that host reacting species. Then, after reaching a critical size, the particles (nuclei) grew individually, adsorbing reacting species on their surfaces and leaving the number of particles constant.

TEM was used to monitor the growth of BaWO\(_4\) nanostructures using a block copolymer poly(ethylene glycol)-block-poly( methacrylic acid) (PEG-b-PMAA) in cationic reverse micelles.\(^{104}\) Penniform (brush-like) nanostructures made of nanowires or nanobelts were obtained by variation of the synthetic conditions. It was observed that in
the absence of the polymer, well-defined bipyramid nanostructures were formed. In PEG alone, deformed bipyramid structures were formed, while the use of 0.2, 0.4, and 0.8 g/L PMMA resulted in shuttle-, peanut-, and sphere-shaped nanocrystals, respectively. Thus, it was determined that PMMA played a significant role in the directed growth of the nanostructures, while the role of PEG was primarily to promote solubilization in water. Monitoring the growth of the nanostructures under different conditions leads the authors to propose a two-stage growth mechanism as shown in Scheme 2.

Scheme 2. Schematic of the Mechanism for the Growth of Penniform BaWO₄ Nanostructures

(a) Stage 1 (polymer-controlled)

(b) Stage 2 (surfactants controlled)

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In the first stage (stage 1, Scheme 2a), the polymer induced the formation of shuttle-like nanocrystals that were oriented along the c-axis. These shuttle-like nanocrystals subsequently attached with one another in a directed manner, resulting in the formation of [100]-oriented shafts that had many parallel needle-like structures oriented along the [001] direction, i.e., perpendicular to the [100]-oriented shaft. Stage 2 was surfactant-controlled (Scheme 2b) as, at this stage, the polymer had been substantially depleted from the reaction mixture. In this stage, well-defined penniform BaWO₄ nanostructures were formed by the evolution of the needle-like structures (along [001]) into nanowires or nanobelts. The ratio of cationic to anionic surfactants, r, determined whether a nanowire or nanobelt was formed. When r = 1, nanowires were formed, while at r deviating from 1, nanobelts were formed.

Most of the earlier reports were from a chemist’s perspective. However, lab-scale synthesis has its own limitations in terms of scalability and, thus, commercial viability. Many of the surfactants used for these studies are expensive and not of practical application in bulk production. Sundmacher’s group pioneered the mechanistic studies of synthesis of barium sulfate nanoparticles in an industrial-scale reactor using the water-in-oil microemulsion method with cyclohexane as the oil phase and an inexpensive nonionic surfactant Marlipal O13/40 (an alkyl polyethylene glycol ether). Barium sulfate is an important chemical due to its whiteness, inertness, and opaqueness to X-rays and has applications as a radiocontrast agent, filler in plastics, extender in paints, and additive in pharmaceutical products and printing ink. By variation in mixing conditions of the starting materials, barium chloride (feed) and potassium sulfate (reactor), the morphology and size of the nanoparticles obtained were varied as observed by TEM.

A previous work by the same group had demonstrated that the final particle size and morphology were strongly dependent on the initial concentration difference between the reactor and feed (C₀). Below C₀ of 0.075 mol/L, there is almost no variation in particle size of ~6 nm; at C₀ > 0.075 mol/L, the particle size and morphology may be varied by controlling other parameters. The authors in an extension of this previous work investigated the effect of particle size and morphology by variation of C₀ and feeding strategy. The feeding strategy included variation in feeding rate and addition of feed in small batches with intervals between the batches (pulsed feeding). These variations in C₀ and feeding strategy resulted in three different particle shapes according to the experimental conditions, namely, spherical, plate-like with a main quadratic/rectangular face (rectangular rhombohedra), and plate-like with a main hexagonal crystal face (polyhedra). When C₀ < 0.075, spherical particles with a size of ~6 nm, which incidentally corresponded to the size of the micellar droplets. Higher C₀ values lead to plate-like (hexagonal- or rectangular-faced) particles whose size was much larger. A linear relationship existed between the particle size and particle thickness.

This difference was attributed to different mechanisms. The droplet size and surfactant monolayer influenced the first stage of particle formation with the particle size being limited by the droplet size and independent of C₀ and the feeding strategy. The particle formation was very fast and the formation rate was limited only by the rate of droplet exchange. For the formation of larger particles, it was argued that the size barrier had to be crossed and the particle/surfactant layer had to be destabilized. It was postulated that the difference in feed concentration to the concentration of the reactant results in an increase in electrolyte concentration and hence decreased solubility of the surfactant in water, ultimately leading to a less stable micelle and a larger particle. The growth of the particles was demonstrated to occur by coagulation as opposed to Ostwald ripening as the dissolution of the smaller particles necessary for Ostwald ripening was not observed. The authors did not pinpoint the exact principle governing the formation of different faces (hexagonal or rectangular), but several possible explanations from the literature were presented. Overall, the phenomenon was attributed to different growth laws for the individual faces. At C₀ > 0.075 (beyond the growth barrier), small feed rates resulted in large nanoparticles with a high polydispersity. This was explained on the basis of the time progression of the growth of the particles. Particles formed earlier, break the growth barrier, and form hexagonal main face particles, while those formed later were limited by the availability of reactants and did not grow beyond the rectangular main face. A pulsed feed resulted in multimodal particle size distribution with a low polydispersity of the individual subpopulations.

4.3. Noble Metal Nanoparticles. The growth mechanism of Au NPs by using the RM method was investigated by XAFS, SAXS, DLS, UV–vis, and TEM. Previous SAXS and XANES studies by Polte et al. on Au NPs that were formed on reduction by citrate ions (that stabilized it too) report that the reduction proceeds via (1) initially fast formation of small Au nuclei consisting of a few atoms, followed by (2) formation of NP by coalescence of these small nuclei, and (3) ongoing reduction of precursor, resulting in slow growth of NP,
followed by (4) complete consumption of the precursor species via fast reduction. The key step was determined to be the coalescence of the nuclei that resulted in observed dispersity of the nanoparticles. However, better control of dispersity was obtained using the block copolymer (poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide), also known as PEO−PPO−PEO, that, like the citrate ion, played the dual role of a reductant and stabilizer. The mechanism was deduced to be as follows: (1) the polymer facilitated the reduction of the metal ions to form small clusters consisting of a small number of atoms, (2) the polymer adsorbed on the cluster surface and reduced the [AuCl4]− ions that were adsorbed on the surface of these clusters, and (3) steps 2 and 3 iterated until the NP stabilized. The key processes that were found common in these mechanisms were that the metal ions reduced into a cluster and the subsequent coalescence of these clusters.

In the study by Decarolis et al., Au NPs with a final size of ∼60 nm were synthesized using p-toluene sulfonil hydrazide as a reductant and using poly(styrene-b-2-vinyl pyridine) (PS-b-P2VP)-block-copolymer P18226-S2VP as the stabilizer. The reductant used allowed for the rate of the reaction to be “slow” enough to be monitored by instrumental techniques. In situ XAFS was used to monitor the variation in the electronic structure of Au species during the reduction process, while EXAFS through detection of the Au−Au scattering pair evolution was used to follow the formation of Au clusters. In a parallel experiment, HCl was added to remove the excess reductant. The mechanism deduced is summarized in Scheme 3. At the beginning of the synthesis, the micelle core is loaded with the gold precursor (stage 1, Scheme 3). The XAFS data showed predominantly Au−Cl species by which the authors concluded that Au was present as a [AuCl4]−-N (from pyridine) complex, which was dispersed homogeneously over the micelle cores. After addition of the reductant (stage 2, Scheme 3) on the basis of the XAFS results, it was concluded that immediate reduction of the [AuCl4]− ions to the Au(I) species, [AuCl3]−, takes place. SAXS data indicated that the core diameter remained the same at 13.4 nm for the sample without addition of HCl and 16.2 nm for the sample containing HCl. After 2.25 h (stage 3, Scheme 3), the formation of AuI species was observed for the sample containing HCl and low EXAFS-derived values of coordination numbers (C.N.,Au−Au) indicated that it was likely comprised of small clusters. SAXS data showed an increment in the NP diameter during this reduction process, indicating the self-assembly of gold clusters into the NPs. This process of swelling of the micelle core was observed until Au reduction is complete. An excess of Au(I) results in no Au(0) being seen by XAFS; however, a small plasmon peak was seen in the UV−vis spectrum. UV−vis and TEM confirmed further agglomeration of the gold clusters to form NPs (stage 4 in Scheme 3). From the XAFS, UV−vis, and SAXS data, it was postulated that the presence of HCl catalyzed the reduction process of Au(I) to Au(0) and its agglomeration.

The mechanism for the synthesis of Ag and Pd NPs via photoreduction was investigated using UV−vis, TEM, QXAFS, and SAXS in the water/benzene/AOT w/o microemulsion system using benzophenone as a photoactivator. Using n-heptane, n-octane, n-decane, and isooctane, the effects of variation in the oil phase were explored. The UV−vis spectra indicated a minimal effect of solvent on particle size on either Ag or Pd NP. Monitoring the XANES spectrum, it was seen that as time progressed, the peak corresponding to Ag−O decreased and that corresponding to Ag−Ag increased. The coordination number of Ag increased from ∼3.8 to 1.4, while that of metallic Ag bonded to other Ag increased to ∼5.0 to 6.0. Similar observations were made in the case of Pd. An important point to note is that absorbance μ(E) exhibited no contribution of Pd(I) complexes during the photoreduction of Na2PdCl4 and it was postulated that the unstable Pd(I) species undergoes disproportionation to Pd(II) and Pd(0) and, thus, Na2PdCl4 precursors reduced directly to Pd(0) atoms (or Pd...
The trends in coordination number (C.N.) for Pd were similar to those observed for Ag. The C.N. for Pd bonded to Cl decreased from 4.0 to 2.0, while that of Pd bonded to Pd increased to 4.0 as the reaction progresses. The time progression of normalized X-ray absorption was monitored and it was observed that the consumption of Ag⁺ species exactly mirrored the generation of Ag(0) species. For both Ag and Pd cases, in the initial period (up to ∼7000 s), the curve exhibited a pseudosigmoidal profile that was typical of an autocatalytic surface growth and subsequent aggregative growth. A rising slope in the later parts indicated a diffusion-limited Ostwald ripening. The kinetic parameters were calculated by fitting to the Avrami–Erofeev model.

Based on the observations, a mechanism was proposed as depicted in Scheme 4. On photoexcitation of BP, a benzophenone triplet was generated that on abstracting, an H atom from ethanol produced a benzophenone ketyl radical (BPK) and ·C₂H₅OH radical. The ·C₂H₅OH radical, in turn, reduced another BP, leading to the formation of a second BPK radical. Continuous irradiation of aqueous Ag(I) or Pd(II) precursor solutions containing BPK resulted in photoreduction of the metal ions by electron transfer, resulting in the formation of Ag and Pd metals. Subsequently, in the presence of BP, particle growth occurred once the metallic nucleus was formed (autocatalytic surface growth process). Thereafter, larger metal nanoparticles were formed by consecutive aggregative particle growth and Ostwald ripening.

Pileni et al. synthesized Pt nanocrystals by both the phase transfer method and RM method to compare the two methods and gain mechanistic information. It was observed that the former method produced a spherical NP with a diameter of 1.7 nm, while the latter produced a mixture of 75% spherical and worm-like NPs with a cross-sectional diameter of 2.6 nm. The difference in shape of NP produced by the two methods was attributed to the difference in time of addition of the stabilizing agent. In the PT method, the stabilizing agent was part of the reactant and prevented the coalescence of the spherical NP, while in the latter, the addition of the stabilizing agent after an hour permitted the assembly of these spheres into worm-like structures. It was demonstrated that there was no simultaneous growth of spheres and worm-like structures.

The early stages of the formation of bimetallic Pd/Pt clusters were monitored by in situ XAS. In situ XANES and EXAFS analyses for both the Pd K-edge and Pt LIII-edge revealed the formation of Pd/Pt bimetallic clusters. In the first step, Pd clusters were synthesized. The changes in the coordination number C.N., bond distance R, Debye–Waller factor, and inner potential shift were monitored by observing the Pd K-edge via EXAFS during the formation of Pd clusters. N₁₄ decreased on addition of the reducing reagent and, gradually, the N₁₄ contribution appeared, indicating the formation of Pd clusters. The effect was accentuated by further addition of the reducing agent hydrazine. The size of the clusters was determined to be between 1.5 and 2.0 nm. A three-stage mechanism was proposed (Scheme 5a) where, in the first stage, the ME system comprised of Pd⁴⁺, Cl⁻, and SO₃²⁻ (from AOT), which on addition of the reducing agent in the second stage, further addition of the Pd(0) ions. In the third stage, on further addition of the reducing agent, it resulted in complete reduction of Pd(II) ions to Pd(0). On addition of the Pt⁴⁺ ME to the system, bimetallic Pd/Pt clusters form, whose mechanism is shown in Scheme 5b. In the first step, Pd(0) clusters were present along with SO₃²⁻ from the surfactant. On introduction of the Pt⁴⁺ ME (reaction I, Scheme 5b), a portion of Pd(0) dissolved and Pd–Cl bonds as well as [PtCl₄]²⁻ complexes were formed (stage B, Scheme 5b). On addition of the reducing agent (reaction II), Pd–Cl and Pt–Cl bonds transformed to the respective hydroxides (stage C, Scheme 5b), indicating that both the metallic cores underwent ligand exchange. Particle growth occurred via MED collision, fusion, and exchange of products. Further addition of hydrazine resulted in the formation of Pt–Pd and Pd–Pt bonds with partial Pt–OH persisting in the reaction mixture (reaction III). Bimetallic clusters were observed in the final step (reaction IV). Further, the EXAFS data showed that in the alloy clusters, the Pt atoms were situated more toward the outside surface and were more prone to more clustering than the Pd atoms (Scheme 5c). This observation is very relevant to catalytic applications. An extension of this work to investigate the distribution of metal atoms on variation of anisotropy may yield interesting mechanistic information.

4.4. Sulfide Nanoparticles. The mechanism of growth of ZnS nanoparticles using the MED method templated by block copolymer poly(styrene)-b-poly(2-vinyl pyridine) was investigated by SAXS and high-resolution analytical transmission electron microscopy (ATEM). Zinc acetate was added to PS-b-P2VP micelles that were expected to form a block ionomer micelle, in which the Zn²⁺ ions coordinate via dative bonds to the P2VP moieties that form the core. Exposure of these block ionomer micelles to H₂S gas, ZnS

Scheme 4. Mechanism of Formation of Ag and Pd Nanoparticles Synthesized in the Presence of Benzophenone

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nanoparticles were formed. It was observed that small crystallites (∼4 nm) existed within a larger (∼20 nm) amorphous organic–inorganic hybrid matrix. The crystallite phase that consisted of a large fraction of the nanoparticle volume was characterized by bright-field HR-TEM to be cubic sphalerite ZnS and consisting of small irregularly shaped nanocrystallites distributed throughout the nanoparticle. It was observed that the thermodynamically favorable crystalline phase does not grow in size with time and, hence, the possibility of it being formed by slow transformation from the amorphous phase (which may have formed from rapid precipitation) was discounted. It was determined that the amorphous phase was in fact not pure ZnS but a hybrid phase of ZnS and P2VP. It was postulated that initially, Zn²⁺ ions complexed with the pyridine moieties are spread over the entire P2VP micellar core. On sulfidation, these ions are bridged; however, phase separation was not induced, thus effectively immobilizing the P2VP in the ZnS phase and forming an amorphous hybrid structure. The regions of crystalline growth within these amorphous regions were

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postulated by either random nucleation of crystalline ZnS or the existence of nanometer-sized regions within the micellar core that had high Zn$^{2+}$ concentration. Use of a large-angle EDX detector to collect rapid EDX data was used to prove this hypothesis.

The implication of this mechanism is that the size and morphology of the final nanoparticle would mirror the micelle core at the point of sulfidation. SAXS was used to study the three stages of NP formation, (1) the block copolymer micelles, (2) the metal-loaded block ionomer micelles, and (3) finally, the obtained NP. As expected, the morphology (spherical) and size of the block ionomer micelle were found to mirror those of the final NP, thus validating the mechanism. Another observation that supported this mechanism was that the NP size decreased with the increase in the amount of Zn added. It was argued that increased loading of Zn$^{2+}$ decreased the micellar core size as a result of dipole—dipole interactions of the P2VP-Zn$^{2+}$ complex.

In contrast, using the same conditions for the preparation of Au NP, it was observed that the radius of the Au NP is much smaller than the core size of the micelle. Additionally, the size of the Au NP increased on increasing the Au precursor loading in the synthesis. Thus, different mechanistic pathways existed for the synthesis of ZnS and Au NP stabilized by block polymers. The spherical shape in Au NP was attributed to the minimization of surface energy as opposed to the shape of the block ionomer micelle as in the case of ZnS.

**4.5. Fluoride Nanoparticles (YF$_3$).** An excellent and detailed investigation on the mechanism of YF$_3$ nanoparticle formation using TEM and colorimetric analysis was reported. Apart from classical microemulsion (ME) where both the Y and F precursors (YCl$_3$ and NH$_4$F$_2$, respectively) were added as an ME (experiment A), experiments were also carried out where NH$_4$F$_2$ was added as an aqueous solution to YCl$_3$ as an ME (experiment B). Additionally, secondary growth experiments were also carried out where, to the suspension of already formed nanoparticles (via experiment B), the following was added: (1) Y and F both added as microemulsion (experiment 1), (2) Y added as an aqueous solution and F added as an ME (experiment 2), (3) Y added as an ME and F added as an aqueous solution (experiment 3), and (4) both Y and F added as aqueous solutions (experiment 4). Different concentrations of precursors were used in experiment 4. In another variation of the experiment, mature particles were added to a growing population (experiment 5).

Experiment A yielded amorphous YF$_3$ particles with sphere-like shape (AmphA). The size increased (6−47 nm) with an increase in water content. In experiment B, a mixture of octahedral single crystal (OhB 20−350 nm) and spherical amorphous particles (AmphB) was obtained. In both experiments A and B, the particles were visible soon after mixing. After 30 min, the amorphous and crystalline particles could be distinguished and, after 4 h, the octahedral shape could be distinguished in the crystalline particles. AmphA reached their final size after 4 h, while OhB and AmphB grew for 24 h and 2 days, respectively. Additionally, smaller particles were obtained with experiment A, indicating the formation of a larger number of stable nuclei.

In the secondary growth experiments (experiments 2−4), it was found that the mode of ion addition influences the composition. When the fluoride precursor was added as an MED (experiments 1 and 2), amorphous particles were formed as in the classical MED method. However, when fluoride was added as an aqueous solution (experiments 3 and 4), a mixture of amorphous and crystalline particles were formed analogous to single ME methods. The mode of addition of YCl$_3$ did not modify the nature of the particles but influenced the secondary nucleation.

Overall, it appeared that nucleation was the crucial step that governed the crystalline or amorphous nature of the YF$_3$ nanoparticles. Additionally, no interconversion between mature particles was observed. It was observed that there must be adequate supply of precursor materials for particles to reach a critical size and nucleate and form particles. This critical size is governed by eq 18 and, below this size, the nuclei would redissolve.

$$\Delta G_{\text{nucleation}} = S + V \Delta G_{\text{crystallization}}$$

where $S$ and $V$ are the surface and volume of the nucleus, respectively, $\gamma$ is the interfacial energy, and $\Delta G_{\text{crystallization}}$ is the free energy of crystallization, which is a function of the reagent concentration and becomes negative as saturation is reached.

The order of introduction of the precursors governed the outcome of the single-microemulsion method. If an aqueous fluoride solution was added to a yttrium-containing ME, then it results in a mixture of octahedral and spherical particles. If the order was reversed, i.e., aqueous yttrium solution was added to a fluoride-containing microemulsion, then amorphous particles, similar to those obtained by the classical ME method, were obtained.

The single ME method is described in Figure 1B. Initially, the added solution disperses in the organic phase in the form of droplets larger than the ME. These droplets interact with the ME. It was postulated that during the nucleation step, local fluoride excess leads to the formation of crystalline YF$_3$ nanoparticles, whereas an excess of yttrium leads to amorphous particles. In contrast, stoichiometric quantities of fluoride in the classical ME method lead to amorphous particles. It was argued that excess fluoride allowed stoichiometric 3 F$^-$ to surround Y$^{3+}$ during ion assembly. In fluoride-deficient situations, species other than F$^-$ ions are produced and result in amorphous end products. The colorimetric experiments indicate that mixing within the micellar system occurred rapidly within a few seconds. $^{19}$F NMR indicates the absence of free solvated fluoride 40 min after mixing. Thus, it was inferred that the fluoride ions must be present as a bound species to seed the particle growth. Additionally, from experiment 5, it is inferred that the nucleation was complete within the first 2 min.

Two particle growth mechanisms were possible: (1) Ostwald ripening and (b) coagulation. In the former, particle growth fed by the dissolution of small, unstable nuclei (whose concentration is held constant at solubility) occurs slowly and, at a constant rate, while in the latter, two nucleated particles combine to form a larger one. In the Ostwald ripening mechanism, small nuclei that, by virtue of their non-negligible surface energy, redissolve to maintain an adequate concentration of free ions. On consumption, the smaller nuclei particle growth stops. Larger nuclei do not contribute to this mechanism due to lower solubility. However, these larger nuclei can coagulate and, as opposed to Ostwald ripening, the growth is faster due to addition of more materials per collision. Coagulation, however, is still limited to smaller particles as opening up the surfactant layer is energetically unfavorable for larger particles. Higher $W_0$ values result in more flexibility of the surfactant layer and favors coagulation. Although it is
expected that the amorphous and crystalline particles grow at a comparable rate, it was seen that the growth rate of AmphB was five times faster than OhB and consumed 10 times more starting materials. Overall, based on these and other observations, it was concluded that AmphA (from the classical ME method) and OhB (from the single ME method) grew via Ostwald ripening, but AmphB (from the single ME method) grew via coagulation and this difference was attributed to a wider size distribution of the nuclei formed upon mixing in the single ME method.

4.6. Nanotubes of Conducting Organic Polymers. The synthesis of conducting polymer polypyrrole nanotubes using the MED method in the 2O/FeCl₃/AOT/apolar solvent system was investigated. FeCl₃ played a dual role of aiding in the formation of the soft templates as well as in the polymerization of the pyrrole monomers. It was proposed that there was a cooperative interaction between aqueous FeCl₃ solution and the surfactant AOT in an apolar solvent. The metal salts incorporated into AOT emulsions were thought to influence the micelle aggregation number and second critical micelle concentration (CMC II). The number of surfactant molecules required to form a micelle is described by the micelle aggregation number and second critical micelle concentration (CMC II). The Fe cations adsorbed to the anionic AOT headgroups were also capable of extracting metal cations from the aqueous core. Thus, it was postulated that on addition of the pyrrole monomer, chemical oxidation polymerization on the surface of cylindrical MED resulted in the formation of PPy nanotubes.

Increasing the volume of the FeCl₃ solution w.r.t. the surfactant leads to larger water cores and, thus, nanotubes of larger diameter. It was observed that an increase in the hydrocarbon chain length of the apolar solvents leads to an increase in the diameter of the AOT reverse cylindrical micelles. It was argued that apolar solvent molecules with short hydrocarbon chains can penetrate into the palisade layer consisting of hydrophobic AOT double tails, while it is difficult for those solvents with longer tails, thus leading to longer micelles. Additionally, with an increase in temperature, nanotubes with increased diameters were observed and it was argued that this was due to an increase in the chain mobility of the surfactant, which leads to the inability of the solvent molecules to penetrate the palisade.

5. CONCLUSIONS AND OUTLOOK

Anisotropic nanoparticles synthesized through the RM method have been shown to exhibit numerous applications including in catalysis, energy storage, antibacterial agents, and biomedical applications like drug delivery and bioimaging. For example, anisotropic Fe₃O₄ nanorods were developed for Li-ion storage, Pd nanocubes were investigated for their catalytic activity toward Suzuki coupling reactions, rare earth-doped Gd₂O₃ nanorods were synthesized and applied for magnetic resonance imaging, PHEMA-g-(PAA-b-PEG) molecular bottlebrush (MBB) nanoparticles with different anisotropic morphologies were developed and applied for bioimaging and photothermal cancer therapy, and anisotropic PNSAAc [poly(nisopropylacrylamide-co-stearyl acrylate-co-acrylic acid) (poly(NIPAM-co-SA-co-AAc))] and PNSAAm [poly(nisopropylacrylamide-co-stearyl acrylate-co-allylamine) (poly(NIPAM-co-SA-co-AAm))] were nanostructures synthesized for drug delivery studies.

Although there are numerous literature reports on the synthesis and the application of 1D anisotropic nanostructures, there are just a handful among them that carry out mechanistic studies on the growth of these nanostructures and the most important of these were reviewed. From the review, it becomes apparent that the quantum of currently reported work is much less than that needed to generate a set of empirical rules that would govern the synthesis of such nanostructures. Further, only a few types of nanostructures were systematically investigated. It was seen (in the case of ZnS and Au) that with the current know-how in the field, the same experimental conditions do not necessarily translate to a similar mechanism. All these factors essentially prevent this potentially very useful technique to be applied on an industrial scale for a variety of shape-, morphology-, aspect ratio-, and dispersity-tailored nanostructures. As such, the research on mechanistic aspects of industrial-level synthesis by this method is extremely limited, again contributing to increased cost, thus rendering it unviable.

One of the reasons is that this technique has not matured enough for its application in large-scale production of desired nanostructures due to inadequate insights into the mechanistic aspects of the technique. It is therefore very imperative that more and more quality research is undertaken in this direction. It may be noted that the single microemulsion technique that was introduced almost a decade ago has not been fully investigated. It was seen that for the case of YF₃ synthesis, crystalline particles result from the single ME technique as opposed to amorphous particles resulting from the conventional ME. This was due to the excess of fluoride species in the solution that has the probability of interaction with a Y-containing MED, aiding in the formation of a stoichiometric crystalline species. Thus, the single ME technique looks promising as it may be used to produce a good-quality crystalline product while reducing the complexity in synthesis and its mechanistic aspects should be investigated further. However, we understand that the single ME method may not be possible for every nanomaterial.

The stages of the nucleation-dominant growth period until a critical size is reached, a transition period where the switching of the geometry takes place and the elongation of the nanorods occurs, are seen in multiple mechanistic studies. But insights into what triggers the transition are lacking. Processes like time-resolved ultrafast SANS should be employed to get a deeper understanding of this and the other stages of the growth process. The experimental ultrafast spectroscopy techniques along with theoretical studies should be employed to get more accurate timescales and other mechanistic insights into the growth of these anisotropic nanostructures. Additionally, no literature report is available about the mechanistic investigation of core–shell structures that are prepared by the RM method. Another area that needs some investigation is the area of surfactants. All the reports in the literature use permutations and a combination of the same surfactants. Research should be carried out for the synthesis of a library of surfactants with varying properties that may be used to fine-tune the RM-based synthesis. This would aid in industrial application of the method as the cost of the surfactant is a substantial component in the overall cost of synthesis by this method.
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