Preparation of metal nanoparticles in water-in-oil (w/o) microemulsions

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Abstract

The use of an inorganic phase in water-in-oil microemulsions has received considerable attention for preparing metal particles. This is a new technique, which allows preparation of ultrafine metal particles within the size range 5 nm < particle diameter < 50 nm. This article presents a review of the current literature in the field of particle preparation of several metals such as silver, copper, cadmium, cobalt, nickel, cadmium and gold in the inverse microemulsion systems. The reactant metal salts and reducing agents are mostly soluble in water and therefore the nucleation of metal particles proceeds in the water pools of the microemulsion. The rate of particle nucleation is a function of the percolation degree of microemulsion droplets. Besides a short introduction into some aspects of the microemulsion types and formation, we mainly focus on the kinetics of metallic particle formation. Effects of stabilizer (emulsifier) type and concentration and the type of continuous phase, reducing agent and additive on the particle formation are summarized and evaluated. The influence of several other parameters such as temperature, the incident light, the nature of metal salts and reaction conditions are also reviewed. These results indicate that the nature of the stabilizer emulsifier, the surface activity of additives and the colloidal stability of microemulsion droplets play decisive role on the particle size and distribution during the preparation of metal particles.

Keywords: Water-in-oil microemulsion; Metal particles; Particle nucleation and growth

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1. Introduction

Colloidal noble metals are well known and have been used technologically for a very long time now. The red color of colloidal gold, for instance, has been used as coloring agent for glass and enamel, as ‘purple of
Cassius’ [1]. Recently, these materials have received considerable attention since they can offer highly promising and novel options for a wide range of applications [2–4]. For example, due to their nanosize dimensions, gold and silver colloids exhibit interesting optical properties. Metal nanoparticles show peculiar optical, magnetic and electronic properties that bulk solid or isolated molecules do not usually exhibit [5], which may find important applications in material technologies like microelectronics, catalytic systems and chemical sensors. Colloidal particles of coinage metals (Ag, Au, Cu) have been widely employed as nanostructured substrates for surface enhanced Raman spectroscopy (SERS) [6]. SERS spectroscopy is potentially a highly sensitive analytical technique, allowing satisfactory discrimination on the basis of the characteristic vibrational bands of the ligands. For various SERS-active surfaces, including electrochemically roughened metal surfaces, deposited metal layers and crystal island films, metal colloidal suspensions offer significant advantages, such as simplicity of preparation, higher resistance to the damage due to the impact with the laser beam than in solid surfaces and higher Raman enhancement factors. Transmission electron microscopy (TEM) and absorption spectroscopy in the UV–visible region allow the investigation on the shape and size of the colloidal particles. The metal colloidal suspensions undergo aggregation by addition of ligand or aging, and this changes the ligand adsorption and the corresponding SERS spectrum. Great interest exists in the preparation of stable colloidal materials with metal particles obtained by photochemical reduction, i.e. without using chemical reagents.

Polymer-protected noble metal colloids are usually prepared from suitable metal precursors by various in situ reactions, such as chemical reductions, photoreductions or thermal decompositions. The goal is to obtain nanoparticles, narrow size distributions and well-stabilized metal microcolloids. A wide variety of preparative methods for gold colloids are known mostly based on precursors containing gold complexes such as [AuCl₄]⁻, with tetrachloroauric acid HAuCl₄ being the precursor most commonly used. These protective polymers employed should fulfill the following requirements:

- they should be soluble in different solvents and be thermally stable at the temperatures used for the preparation and technical applications of the colloids;
- there should be good protective function of the polymer for the stabilization of metal colloids, therefore good interaction with the metal surface is essential [8];
- the polymer should ideally interact with the metal precursor, for instance by the complex or ion-pair formation.

Polymers commonly used so far for the stabilization of cold colloids are poly(vinylpyrrolidone) and poly(ethylene glycol) and their copolymers [7,9]. Several other groups of polymers can be selected and investigated for their usefulness to stabilize such metal colloids. For example:

Water-soluble homopolymers and random copolymers possessing a hydrophobic backbone to interact with the metal surface and hydrophilic side-groups to interact with the dispersion medium are often used for the stabilization of metal colloids [8]. For these flexible polymers the stabilization of the metal colloids is based on steric effects [10].

Another group consists of cationic polyelectrolytes since they can offer several advantages. First they combine both steric and electrostatic stabilization of colloidal metal particles [10]. They also offer a very good interaction with the metal precursor, here the negatively charged tetrachloroauric acid anion, through ion-pair formation [11]. Furthermore, the gold colloids are known to carry a negative surface charge stemming from adsorbed chloride anions from the precursors [7,9]. These considerations led to the choice of cationic polyelectrolytes as alternative potential stabilizers for colloidal gold nanoparticles.

A third interesting group consists of amphiphilic block copolymers. Not only are they very good steric stabilizers for metal colloids [10], but particle sizes can be controlled as well, due to the possibility of particle growth within the micelles formed [12].

Nanosized semiconductor has been extensively studied in the last decade, because of the novel optical electronic properties arising from the quantum confinement effect, which vary significantly with the size [13]. Nowadays semiconductor nanoparticles as functional materials have many potential applications [14], but the disadvantages of nanoparticles liable to aggregate and uncontrollable size hinder the process. A reverse micelle (microemulsion) method, as a kind of soft technique, is a suitable way for obtaining the uniform and size controllable nanoparticles. The droplet dimension can be modulated by various parameters, in particular W (W = [water]/[surfactant]) [15]. Recent studies indicated that with the assistance of cosurfactant, the size of nanoparticles prepared in quaternary reverse micelle system is more controllable [16]. However, the relationship between W and the nanoparticle size is still inadequate and needed to be further studied. For example, compared with the anionic (bis(2-ethylhexyl)sulfosuccinate, AOT) ternary reverse micelle system, the droplet dimension of the quaternary cationic (cetyltrimethyl-ammonium bromide, CTAB) reverse micelles can be elaborately adjusted by changing W with the additional modulation of cosurfactant at the interface of water and oil. The microstructure and dynamic exchange process are dominated by the influence of cosurfactant.
on the curvature radius and interface rigidity of the droplets in the quaternary reverse micelle [16]. The cosurfactant also can be used as capping reagent to modify the nanoparticles surface effectively and thus improve the photoluminescence efficiency. It is deduced that the quaternary CTAB reverse micelle is an important system to be exploited for the fabrication of nanoparticles.

2. Formation of microemulsions

A stabilizer (emulsifier) is a molecule that possesses both polar and non-polar moieties. In very diluted water (or oil) solutions, emulsifier dissolves and exists as monomer, but when its concentration exceeds a certain minimum, the so-called critical micelle concentration (CMC), the molecules of emulsifier associate spontaneously to form aggregates—micelles. Micelles are responsible for many of the processes such as enhancement of the solubilization of organic compounds in water (oil-in-water (o/w) emulsion) or hydrophilic compounds in the oil phase (water-in-oil (w/o) emulsion). The formation of o/w or w/o micelles is driven by strong hydrophobic interactions of the hydrophobic tail of the emulsifier molecule (o/w micelle) or by hydrophilic interactions of the polar head of the emulsifier molecule (w/o micelle). In the former, the strong hydrophobic interaction between hydrophobic chains arranges a large number of amphiphiles into the aggregate (micelle). Amphiphilic molecules in non-polar solvents do not experience a hydrophobic effect. The force responsible for the association of amphiphiles is directly attributable to the interaction between hydrophiles, and since it is generally sterically difficult to arrange a large number of emulsifier molecules. The characteristic features of the reverse (w/o) micelles are the small aggregation number and indistinct transition from monomer to micellar assembly (critical micellar concentration). They seldom range above 20 and are often much less. In some cationic and non-ionic emulsifiers, the aggregation numbers are quite small, there is no real identifiable CMC, and the aggregation number increases continuously with increasing solute concentration [17]. The emulsifier systems consisting primary of anionic emulsifiers, exhibit larger values of aggregation number (25–30), a CMC is more or less apparent, and the aggregation number approaches a plateau value as the solute concentration is increased [17]. Even the aggregation number of inverse anionic micelles is much smaller than that of direct micelles.

The titration of coarse emulsion by a coemulsifier solution leads in some cases to the formation of a transparent microemulsion structure. The transition from opaque emulsion to transparent solution is spontaneous and well defined. Zero or very low interfacial tension obtained during the redistribution of the coemulsifier plays a major role in the spontaneous formation of microemulsion. As soon as the interface curls and droplets are formed, the interfacial tension increases. Microemulsion formation involves an abrupt increase in the interfacial area. Microemulsions consist of, at least, a ternary mixture of water, a surfactant or a mixture of surface-active agents and oil. Depending on the proportion of suitable components and hydrophilic–lyophobic balance (HLB) value of the surfactant used, the formation of microdroplets can be in the form of oil-swollen micelles dispersed in the aqueous phase as for the o/w microemulsion or water-swollen micelles dispersed in oil as the w/o microemulsion (reverse microemulsion). In the intermediate phase region between o/w and w/o microemulsions, there may exist bicontinuous microemulsions whose aqueous and oil domains are intercon

The packing parameter of emulsifier molecule in the fully extended chain length of the emulsifier. When the ratio \( v/a \cdot l \) is larger than unity, the aggregate curvature will be toward the water. This corresponds to a situation where the oil is penetrating the emulsifier tails and/or the electrostatic repulsion between the charged head group is low. When the ratio is less than unity we have a situation where the electrostatic repulsion is larger and/or the oil is not penetrating the emulsifier tails [20]. Spherical direct micelles are formed when the packing parameter is less than 1/3. The limiting values for packing parameters for cylinders and planar bilayers are \( \frac{1}{2} \) and 1, respectively. Reverse micellar structures are formed within the right solvent when the packing parameter is greater than 2 (cylinders up to \( v/a \cdot l \leq 2 \).
and spherical micelles when \( v/a \cdot l > 3 \). When oil is solubilized in hydrophilic micelles, or water in hydrophobic micelles, one can observe the formation of o/w microemulsions for \( v/a \cdot l < 1 \); or w/o microemulsions for \( v/a \cdot l > 1 \). When \( v/a \cdot l = 1 \), lamellar phases or bicontinuous microemulsions are observed [21]. O/w microemulsions are monodisperse.

W/o microemulsion solutions are mostly transparent, isotropic liquid media with nanosized water droplets that are dispersed in the continuous oil phase and stabilized by surfactant molecules at the water/oil interface. These surfactant-covered water pools offer a unique microenvironment for the formation of nanoparticles. They not only act as microreactors for processing reactions but also exhibit the process aggregation of particles because the surfactants could adsorb on the particle surface when the particle size approaches to that of the water pool. As a result, the particles obtained in such a medium are generally very fine and monodisperse [22]. Inverse microemulsion droplets, however, are slightly polydisperse due to less strict transformation of monomer to assembly form (see above). The microemulsion is thermodynamically stable phase and therefore the polydispersity is an equilibrium property. The droplets collide, form transient aggregates and then revert to isolated droplets. Aggregate lifetimes are typically of the orders of microseconds. The dynamics of the exchange of solute between micelles and the continuous phase is characterized by the rate constant for entry of the solute into the micelle. This process is diffusion controlled, as is the entry of emulsifier molecules into the micelle. Under certain critical conditions, molecules can be transported from one droplet to another without going through the continuous phase. A possible process involves collisions and transient merging of the droplet cores. At low concentration of the dispersed phase, the dispersion is mostly composed of identical spherical isolated droplets. At higher concentrations, the structure of the system depends on the interactions between droplets. If they are repulsive, the collisions are very short and no overlapping between interfaces of colliding droplets occurs. If the interactions are attractive, the duration of collisions increases, and transient clusters of droplets are formed. Interfaces overlapping occur during collisions, allowing exchanges between touching droplets. These exchanges are achieved by hopping of ions or molecules through the interfaces, or by transient opening of these interfaces with communication between the water cores of the droplets. The electrical conductivity of the w/o microemulsion is an ideal approach to study the percolating events. As the continuous phase of w/o systems is not conducting, electrical conduction needs contact of droplets to allow charge transfer between them. This transfer can be achieved by charge hopping, or transient merging of connected droplets with communication between the water cores [23]. The conditions for proceeding of such events are that the droplet interactions are strongly attractive [24]. When this connectivity is achieved, a steep increase of the conductivity is observed, which has been analyzed as the percolation process, with the percolation threshold \( \phi_{\text{per}} \). Under percolation threshold conditions, water pools of inverse droplets can communicate within the microemulsion system.

The transfer of inorganic salts in reverse (w/o) microemulsions has received considerable attention for preparing semiconductor and metal particles [19,25]. One of the powerful techniques for obtaining the ultrafine particles is based on the use of microemulsions as microreactors in order to control the growth of the particles [26,27]. For the purpose of the method described for obtaining ultrafine particles, water-in-oil (w/o) microemulsions used are formed by nanodroplets of water dispersed in oil. The size of the microemulsion droplets can be modified in the range 5–50 nm by varying the relation of the components of the microemulsion (e.g. changing \( W = \frac{\text{[water]}}{[\text{stabilizer}]} \) in the recipe) or by varying the microemulsion itself. Monodispersity of particles and stabilization of particles are very important criteria in controlled synthesis.

The stabilizer (emulsifier) provides sites for the particle nucleation and stabilization of growing particles. Even though conventional emulsifiers are commonly used in the microemulsion reactors, other non-conventional, which include for example reactive emulsifiers, are found to be more efficient and applicable. For example, these surface active molecules can be bound to the surface of particles, which reduces the critical amount of emulsifier needed for the stabilization of microparticles.

3. Preparation of metal particles and their properties

Once the right microemulsions are obtained, the method of particle preparation consists in mixing of two microemulsions carrying the appropriate reactants in order to obtain the desired particles. A schematic picture of this process is represented in Scheme 1. It can be seen that after mixing both microemulsions containing the reactants, the interchange of the reactants takes place (here referred as metal salt and reducing agent) during the collisions of the water droplets. This interchange of reactants is very fast [28], so that for the most commonly used microemulsions it occurs just during the mixing process. The reaction then takes place inside the droplets (nucleation and growth), which control the final size of the particles. Interchange of nuclei or particles between ‘nucleated’ droplets is hindered because it would require the formation of a big hole during droplet collisions and this in turn would require a great change in the curvature of the surfactant film around the droplets which is not favorable energetically. Microemulsions should be cho-
The possibility of this process occurring would be enhanced in the case of the more energetic collisions and if collisions were strongly interactive. Eicke et al. [30] have already shown, using a hydrophilic fluorescer/quencher system that inter-droplet communication is very rapid, and occurs via a transitory ‘dimery’ species, formed as a result of droplet collision. Similar conclusions have been drawn from a study of the Ni\(^{2+}\)(aq)/Murexide reaction in the AOT/water/heptane system [31], in that exchange of reactants was rapid compared with the time of water exchange at the Ni\(^{2+}\) (aq) ion (=1 ms). Generally the chemical reactions of reactants (metallic salt and reducing agent) within the microdroplet are very fast and therefore the rate-determining step in the overall reaction will be the initial communication step of the microdroplets with different reactants. The rate of communication has been defined by a second-order communication-controlled rate constant \(k_{\text{com}}\) expressed in terms of the droplet concentration in the continuous hydrocarbon medium. This rate constant is then analogous to a diffusion-controlled rate constant in a homogeneous medium, and represents the fastest possible rate constant for the system. The subsequent reaction or the reaction yield then simply serves as an indicator of how fast reactants A and B have communicated. Fisher et al. [32] estimated \(k_{\text{com}}\) to be ca. 10\(^{-6}\)-10\(^{-7}\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) for the AOT/water/heptane microemulsion. This means that approximately 1 in 10\(^3\) of collisions between droplets lead to exchange, since a diffusion rate constant \(k_D\) is ca. 10\(^{-10}\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) in a solvent with viscosity of n-heptane.

When we use anionic emulsifier such as AOT or sodium dodecyl sulfate (SDS) then the interface is negatively charged. The metal cations of their salts will be preferentially located close to this interface, whereas the hydrophilic co-reactants prefer to be located in a region away from the interface. This can lead to the separation of reactants within the larger microdroplet. This separation factor can depress or inhibit the rate of reaction. The same type of partitioning behavior observed for the Ni\(^{2+}\) (aq)/AOT/heptan/Mu\(^-\) microemulsion was also observed with sodium dodecylsulfate micelles [32], but in the latter case the retardation effect is much more pronounced probably due to larger SDS-stabilized droplets or stronger interaction of SDS anion with metal cation. In microemulsions with a small water pool (W<5) no effective separation within a pool can

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**Scheme 2. Proposed percolation mechanism.**
structure and a way of micellar synthesis, in the course of which the desired particles, thereby decreasing their usability. The colloidal stability is adsorbed on the surface of the nanoparticles. Another drawback is that the surfactant ensuring colloidal stability is limited for the amount of organic solvent used. The systems serving to control particle growth are themselves nanostructured (micelles, microemulsions, interlamellar space of clay minerals, etc.), just like the particles to be synthesized. The procedures most widely used are described in Scheme 1. The average size of the nanoparticles synthesized by the microemulsion method depends on the size of the microemulsion droplet, which is determined by the water-to-surfactant ratio (W) [35].

A common way to achieve a uniform particle size is to carry out the synthesis in the interior of small microemulsion liquid droplets [36,37]. For example, metallic nanoparticles were produced in microemulsions by combining adequate amounts of organic solvent, water and surfactant, a precursor of metal ions and reducing agents. One of the disadvantages of this method lies in its expensiveness due to the large amounts of surfactant (as much as 20–30%) added to the system. Another drawback is that the surfactant ensuring colloidal stability is adsorbed on the surface of the nanoparticles, thereby decreasing their usability. The disadvantages may be circumvented by the application of micellar synthesis, in the course of which the desired reaction takes place in the interior of the micelle. When long-chain surfactants are used, micelles with diameters of 2–10 nm are formed which incorporate substantially less surfactant than with the classic method.

The most obvious way to circumvent the above-mentioned problems is to decrease the amount of surfactant or event to avoid the use of surfactants at all. In the former case the covalently bound hydrocarbon tails of surfactants to the particle surface increase the stability of dispersion and the stable dispersion can be obtained even at a relatively small amount of stabilizer. In the latter case particle synthesis may be controlled by two-dimensional structures, for example, the layers of clay minerals [38]. These themselves are nanostructured systems and their lyophilicity and basal spacing can be modified by the incorporation of alkyl chains. The monodispersity of nanoparticles grown in the interlamellar space is attained by stopping the supply of reagent; otherwise, the increasing voluminous particles of various sizes will push the lamellae apart [36].

One problem of using w/o microemulsions for nanoparticle synthesis is the separation and removal of some (highly-boiling point) solvents from products. For example, supercritical carbon dioxide (CO\textsubscript{2},scrit) offers several advantages over conventional organic solvents including: (i) being one of the most environmentally friendly and low-cost solvents available; (ii) rapid separation of dissolved solute from the solvent by reduction of pressure; (iii) providing high diffusivity and thus accelerated reaction rate; and (iv) tunable solvent strength through manipulation of the density and thus providing some control of the solubility of solutes.

Precipitation of metal particles in the reverse micellar system has been found to be as the simple methodology of the simple production of nanoparticles [39,40]. The nanoparticles prepared need to be recovered from reverse micelles and immobilized onto stable supports. One of the most attractive methodologies for the processing of nanoparticles is direct recovery and immobilization by using thiol-modified supports via chemical bonding. For example, thiol-modified mesoporous silica [41] and thiol-modified polystyrene particles [42] were utilized, and the CdS particles, prepared in reverse micellar systems, were successfully immobilized on the supports, by the simple addition of the supports into the micellar solution under conditions of mild stirring.

The synthesized metal nanoparticles can be collected by different methods. Ji et al. [43] used the RESS (rapid expansion of supercritical solution) method [44] to collect the silver nanoparticles synthesized in the water-in-CO\textsubscript{2} microemulsion using NaBH\textsubscript{4}OAc\textsubscript{3}, as the reducing agent. TEM pictures of the collected silver nanoparticles showed an average size of approximately 5–25 nm, larger than the calculated size based on the spectroscopic information. The results suggest that the
RESS method might cause aggregation of the particles during expansion, resulting in a wider size distribution.

Ohde et al. [45] used an in situ deposition method by reducing the pressure of the system to the cloud point of the microemulsion, so that the silver nanoparticles in the microemulsion would precipitate on a solid surface. The particle size of the silver nanoparticles collected by this method appears similar to that collected by the RESS method, that is, approximately 5–25 nm in diameter. Thus, aggregation of the nanoparticles apparently took place during the internal deposition process.

Most of the works about organic–inorganic hybrids (OIHs) focus on polymer nanocomposites in the form of films or bulks. There are two main techniques to prepare them. One is to disperse the preformed nanoparticles, usually after modification with suitable surfactants, in polymer or polymeric monomer solution. For example, Mark et al. [46] prepared monolithic poly(methyl methacrylate)/SiO nanocomposites by dispersing surface-modified silica nanoparticles in methyl methacrylate, followed by polymerization of the monomeric continuous phase. Tang et al. [47] produced a superparamagnetic nanocomposite free-standing film with appreciable electrical conductivity, which was derived from the dispersion of ultrafine Fe₂O₃ particles coated by anionic surfactants in the polyaniline solution. The film was found to possess a saturation magnetization of 25 emu/g γ-Fe₂O₃. Surface modification of nanoparticles used in this method, however, affects surface structure and makes surface and interface activity of the nanoparticles passive. The other technique is to directly create nanoparticles in a hydrocarbon solution containing the polymer or polymeric monomers. For example, Rajeshawar et al. [48] succeeded in dispersing Pt nanoparticles in polypyrrole thin films using a modified electrochemical method.

### 3.1. Iron nanoparticles

A simple and powerful method for obtaining ultrafine iron particles by means of chemical reactions is the microemulsion media [49]. As an example, in Fig. 1 some particular results for iron particles were obtained in the AOT microemulsions with a stopped-flow technique. Both the nucleation and growth processes can be clearly seen. Nucleation implies an increase in the number of scattering centers, which is associated with the increase of the scattering intensity. On the contrary, the growth of the particles is associated with a decrease of the scattered intensity.

Transition electron microscopy (TEM) micrographs of particles after precipitation and drying show that the particles are kept apart because of the surfactant molecules attached to their surfaces. The presence of surfactant was seen in X-rays spectrum. This analysis showed, apart from the iron peak, the S and Na peaks corresponding to the surfactant AOT. The size of Fe particles estimated by TEM is ≈4 nm, which is similar to the droplet size of the microemulsion employed (=3.4 nm). Some of results for the radius of particles (rₚ) obtained by dynamic light scattering (DLS) and also by small-angle X-ray scattering (SAXS) for different microemulsions and different concentrations of reactants are shown in Table 1.

All these results show that the size of the particles obtained is in the range of the size of the droplets of the microemulsion used. The final size, however, does not depend, in general, only on the size of the microdroplets, and the other factors, such as concentration of reactants (especially surfactant), flexibility of the surfactant film, etc., may influence the final size of the particles [50]. The size of magnetic particles, such as Fe, has a big influence on their magnetic properties. For example, Fe particles with the average size r ≈3.4 nm show a typical supermagnetic behavior due to their very small size.

### Table 1

Colloidal parameters of AOT-microemulsions for different concentrations of reactants

<table>
<thead>
<tr>
<th>#</th>
<th>[AOT] (mol/dm³)</th>
<th>W</th>
<th>[FeCl₂]×10⁴ (mol/dm³)</th>
<th>[NaBH₄]×10³ (mol/dm³)</th>
<th>rₚ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>22</td>
<td>7.5</td>
<td>3.5</td>
<td>3.9</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>22</td>
<td>3.8</td>
<td>1.75</td>
<td>3.9</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>22</td>
<td>1.6</td>
<td>0.68</td>
<td>4.1</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>22</td>
<td>0.38</td>
<td>0.35</td>
<td>3.9</td>
</tr>
<tr>
<td>5</td>
<td>0.05</td>
<td>10</td>
<td>0.93</td>
<td>0.35</td>
<td>2.5</td>
</tr>
<tr>
<td>6</td>
<td>0.025</td>
<td>4.44</td>
<td>48</td>
<td>24</td>
<td>1.9</td>
</tr>
<tr>
<td>7</td>
<td>0.025</td>
<td>8.88</td>
<td>48</td>
<td>24</td>
<td>2.5</td>
</tr>
<tr>
<td>8</td>
<td>0.025</td>
<td>13.3</td>
<td>48</td>
<td>24</td>
<td>3.3</td>
</tr>
<tr>
<td>9</td>
<td>0.025</td>
<td>17.8</td>
<td>48</td>
<td>24</td>
<td>4.3</td>
</tr>
<tr>
<td>10</td>
<td>0.025</td>
<td>22.2</td>
<td>48</td>
<td>24</td>
<td>4.7</td>
</tr>
<tr>
<td>11</td>
<td>0.025</td>
<td>26.6</td>
<td>48</td>
<td>24</td>
<td>5.4</td>
</tr>
<tr>
<td>12</td>
<td>0.025</td>
<td>31.1</td>
<td>48</td>
<td>24</td>
<td>5.8</td>
</tr>
</tbody>
</table>

*SAXS: runs 1–5, DLS: runs 6–12.*
small size. When size is increased, a transition to the classical ferromagnetic behavior is observed (for \( r_{\text{particles}} \approx 3.4 \text{ nm} \)). The iron boride nanoparticles were prepared by the reduction of Fe(III) salt but the dependence of the average particle diameter on the water and salt concentrations was somewhat complex [51]. As another different magnetic example it was shown the production of a typical iron-rich spinel: magnetite. An aqueous solution \( /n\)-heptane/\( /AOT\) \( (W=10)\) microemulsion containing \( FeCl_2 \) and \( FeCl_3 \) was mixed with another similar microemulsion containing \( NH_4OH\). The X-ray diffraction pattern of separated (washed and dried) product indicates the presence of \( Fe_3O_4\). The hysteresis loop at room temperature of the powders obtained show that the particles are supermagnetic due to their small size \( (r_p \approx 4 \text{ nm})\). An aqueous solution/\( /\text{ethyl oleate/} \) (labrasol/isostearic plurol) microemulsion containing \( FeCl_2 \) and \( NiCl_2 \) was mixed with another similar microemulsion containing \( \text{NaBH}_4 \) to obtain FeNi alloys. The magnetic properties of these samples measured in a magnetic field of \( Oe \) at room temperature (grain size \( \approx 30 \text{ nm} \approx \text{droplet size} \) are: magnetization, \( M=4.2 \text{ emu/g} \) and coercive field, \( H_c=10 \text{ Oe} \).

The preparation of metallic iron/gold nanoparticles takes advantages of two self-organizing processes [52]. First, the authors employ the reverse micelle method to synthesize metallic nanoparticles in the water pools of the reverse micelles. Metallic nanoparticles are synthesized in reverse cetyltrimethyl-ammonium bromide (CTAB)/butanol/octane/water microemulsion solution using hydrazine as a reducing agent. CTAB acts as surfactant and butanol as cosurfactant. Hydrazine is injected into the solution reducing Fe(II) to Fe(0). The metallic iron particles grow to fill the centers of the micelle and minimal aggregation of iron occurs since the organic portions of the micelle keep particles separate. In a second self-organizing process, since gold and sulfur form spontaneous bonds, the gold coating will direct the ferromagnetic nanoparticles into an ordered array on the surface of a thiol functionalized substrate to produce a thin film. Once the iron particles have formed inside the micelle, an aqueous solution of \( \text{HAuCl}_4 \) is added to the iron/CTAB mixtures. Addition of the aqueous gold solution increases the size of the reverse micelle and the Au (II) is reduced to Au(0) via excess hydrazine. Because gold and iron grow with complementary crystal structures, the metallic gold forms a coating on the outer surface of the iron particles. The gold shells on the iron particles provide functionality and thin films of the gold coated particles have been made by self-assembly reactions between the gold surface of the particle and thiol functionalized substrates. Multilayers of gold coated iron nanoparticles can be formed by additional self-assembly reactions. An X-ray diffraction pattern obtained on a powder sample of gold coated iron shows that only gold and iron exist in the sample and the 2.5-nm thick gold coating effectively prevents any oxidation of the metallic iron core. TEM images illustrated differences between samples prepared in two different ways. The first image was obtained with a drop of methanol suspension of 15 nm metallic particles, which showed the aggregation of particles due to attraction of magnetic cores. No aggregation is noticed in the sample containing a thiol functionalized grid.

Magnetic measurements performed on powdered samples of gold coated iron nanoparticles illustrate that the gold has a minimal effect on the magnetic properties when compared to that of pure iron. The only difference in the properties for the iron and gold coated iron lies in the permanent magnetization. The smaller moment of 18 emu/g for the gold coated iron is due to the additional non-magnetic mass of gold as compared with 22 emu/g for pure 15 nm iron. From the Scherer equation, the magnetic grain size is estimated as 12 nm. This is in excellent agreement with a total particle size of approximately 15 nm as the gold coating is expected to be approximately 2.5-nm thick.

3.2. Platinum nanoparticles

The effect of emulsifier type and temperature on the kinetics of the formation of platinum nanoparticles in w/o microemulsions by chemical reactions of \( PtCl_6^{2-}\) were examined with time-resolved UV–Vis absorption spectroscopy [53]. The platinum particles were prepared in microemulsions containing \( /n\)-heptane as oil phase, water and emulsifier. The surfactant used were poly(ethylene glycol)monododecyl ethers \( (C_{12}E_y \text{Brij} 30), C_{12}E_5, C_{12}E_y \) \( y\). AOT and mixtures of the alcohol ethoxylates and AOT. \( /n\)-Heptane and the emulsifier were mixed and an aqueous solution of the Pt complex \( [Pt^{IV}\text{Cl}_6]^{2-}\) was subsequently added to form a microemulsion with the Pt complex in the water pools. The water-to-emulsifier molar ratio was equal to 4 and the aqueous component contained 0.2, 0.5 or 3 wt.% Pt. The reducing agent (NaBH\(_4\)) containing microemulsion was then added to the microemulsion with the Pt complex, in an amount corresponding to 5 moles of NaBH\(_4\) per mole of Pt, whereby the Pt complex was reduced to Pt particles. Since reduction of \( PtCl_6^{2-}\) by diffusion of BH\(_4^-\) through the oil continuous domain is rather unlikely, the fusion of droplets is a prerequisite for the reaction to proceed and may be the rate-determining step in the reduction of \( PtCl_6^{2-}\) to metallic platinum. Alternatively, the difference in rate of particle formation may be due to a difference in the microenvironment within the fused water droplets of the microemulsion that form after mixing of the two reactant systems. The rate of droplet fusion is likely to be governed by the type of emulsifier that forms the palisade layer at the oil–water interface. However, it is...
not self-evident which of the two types of emulsifiers, AOT or an alcohol ethoxylate, would give the highest rate of fusion. The anionic emulsifier AOT is much less soluble in the continuous hydrocarbon domain than the non-ionic emulsifiers used. The high solubility of the alcohol ethoxylates in the continuous domain will lead to a flux of emulsifier molecules back and forth between the bulk hydrocarbon domain and the droplets interface. This process will work against tight and ordered packing of alcohol ethoxylates and can consequently be expected to favor droplet fusion. In contrast, the water droplets stabilized by AOT can be regarded as hard spheres, which may lead to more elastic collisions and slower rate of fusion of droplets [54]. The platinum particles were found to be less than 5 nm in average diameter, which was consistent with the microemulsion droplet size.

The chemical reaction of hexachloroplatinic acid (H₂PtCl₆) by NaBH₄ has been suggested to proceed via the following overall reaction in aqueous solution [55]:

\[
\text{H}_2\text{PtCl}_6 + \text{NaBH}_4 + \text{H}_2\text{O} \rightarrow \text{Pt} + \text{H}_3\text{BO}_3 + 5\text{HCl} + \text{NaCl} + 2\text{H}_2
\]

The authors [29] claim that platinum microcrystals catalyze the decomposition of NaBH₄ and consequently, a large excess of NaBH₄ is needed to completely reduce H₂PtCl₆. The ratio of five moles of NaBH₄ per mole of H₂PtCl₆ is probably sufficient for the reduction in non-ionics-, AOT-C₁₂E₈-, and AOT-C₁₂E₆-based microemulsions since the absorbance decay of PtCl₆²⁻ is close to exponential. This indicates that the reaction is of first order and hence limited by the PtCl₆²⁻ concentration. However, the higher reaction order is obtained for the reduction in AOT- and AOT-C₁₂E₈-based microemulsions, implying also that the supply of BH₄⁻ is limited and hence influences the reaction rate for these systems. When the reaction occurs in the water droplets in an AOT-based microemulsion, it is likely that there will be an electrostatic repulsion among the negatively charged AOT sulfonate groups, the hexachloroplatinic complex and the borohydride ions. This repulsion will cause a local increase in concentration of the two negatively charged reactants in the center of the water droplets. An increased reactant concentration can be assumed to cause an increase in reaction time, which has for example been demonstrated for the oxidation of iodide by persulfate using either AOT [56] or sodium dodecylsulfate [57] as emulsifier.

It is also conceivable that the difference in kinetics between the AOT- and the non-ionic-based microemulsions is related to differences in the emulsifier’s ability to act as ligand in the platinum complex. Shelimov et al. [58] suggested different mechanisms for the interaction between PtCl₆²⁻ and alumina, e.g. electrostatic adsorption of the hexachloroplatinic complex at the alumina surface and ligand substitution reactions, where alumina surface groups replace some of the initial ligands in the chloroplatinic complex. In the latter case, both OH-bridging ligands and Cl-bridging ligands are suggested. One can envisage ways in which the emulsifier headgroups, both polyoxyethylene chains of non-ionic surfactants and the sulfonate group of AOT, can interact with the platinum in the hexachloroplatinic complex. The interaction will differ depending on the type of surfactant, and the difference in binding between Pt and the ligands in the complex may influence the kinetics of the reaction inside the droplets.

Colloidal Pt was also synthesized by reducing H₂PtCl₆ with hydrazine in w/o microemulsions consisting of C₁₃E₄(Brij 30)/n-heptane/water [59]. The authors reported the optical properties of nanosized (≈4 nm) Pt particles and related their optical properties to the kinetics of the reaction carried out in their preparation. The absorption spectrum of H₂PtCl₆ in the microemulsion shows two different bands, one centered at 220 nm and the other at 260 nm. When the microemulsion with the reducing agent is added to the microemulsion containing H₂PtCl₆, these bands disappear, and a new peak centered at 236 nm, the only peak in the absorption spectra, appears after a few minutes. These results can be explained by assuming that two different steps are involved during the formation and stabilization of the particles. In the first step, the particles are formed inside the aqueous droplets and the adsorption band (220 nm) lies very near to the theoretical band position in water (215 nm) [60]. In the second step, some kind of interaction between the particles and the microemulsion causes the displacement of the observed band to 236 nm. The band that appears in the optical spectra of Pt in microemulsion, when the salt reduction has been completed, is caused by the electronic surface excitation due to the electric field of the incoming light.

In the series [H₂PtCl₆] = 0.001 M, the sequence of maximum absorption for the samples characterized by \( W = [\text{water}] / [\text{C}_n\text{E}_s] \) values in the range 0.6–6.1 exhibits the red-shift from 246 to 256 (Fig. 2). A possible explanation of this effect can be that as droplet size grows, conditions for surfactant adsorption over the particle surface are more favorable. Surfactant adsorption has been described as proceeding through a series of stages in which the surfactant film has to adopt high positive curvatures [61]. By increasing the droplet size, it is favoring positive curvatures [54] and therefore enhancing the adsorption of surfactant. The wavelength (λₚ) at which a maximum adsorption occurs can be calculated from the Mie theory according to the equation:

\[
\lambda_m^2 = \lambda_c^2 (\varepsilon_o + 2n_o^2),
\]

where \( \lambda = (2\pi c)^2/4\pi N_e e^2 \), \( \varepsilon_o \) is the high-frequency
characteristic of small metallic particles with the surface properties is the very change both the plasma adsorption intensity and spectrum. The sensitivity of the plasma band of particles with the surface properties is the very characteristic of small metallic particles [61].

The aging of solutions causes cluster formation, whose absorption spectrum is rather different from those of the initial solutions with a second smaller maximum at longer wavelengths. The agglomeration of particles may occur upon the aging of solutions that initially contain isolated particles, producing a great change in the absorption spectrum [62]. Even very small amounts of colloid association can alter the UV–vis absorbance [63]. A broad maximum at 302 nm appears several weeks after sample preparation for colloidal Pt reduced in microemulsions, which can be assigned to an agglomeration process. However, after washing and redispersion of Pt dispersion, the 300 nm band is replaced by small and broad maximum at 260 nm. This is consistent with the formation of clusters of particles, because when particles form clusters the absorption spectrum becomes flatter and broader and the maximum appears at higher wavelengths than with isolated particles. This effect is due to the dipole–dipole interaction of the agglomerated particles [64].

Robinson et al. [65] prepared Pt sols in glycerol/AOT/n-heptane microemulsions which showed an increase of the absorbance as the wavelength becomes smaller and a pronounced absorption shoulder at 460 nm. They suggested the possibility of formation of very small Pt clusters with different electronic properties from those of larger particles in order to explain the shoulder. A quantitative relationship between \( \lambda_{\text{max}} \) and size is not known, but qualitatively, for spherical colloids, the work [66] suggests that it is blue-shifted to smaller wavelength with decreasing of the particle diameter.

Microemulsions containing only Pt salt were exposed to daylight for several days, and only after more than 1 month small changes in the spectra were measurable. But when microemulsions are exposed to daylight and kept at the same time in a thermostatic bath at 50 °C, the process is strongly accelerated, and a typical brown color appears after only few minutes. It should be mentioned that Barnickel et al. [67] have also synthesized Ag colloids in \( \text{C}_{12}\text{E}_5/\text{cyclohexane/water} \) microemulsions only using daylight irradiation of the AgNO\(_3\) dissolved in this system. They explained their results, assuming that the terminal hydroxyl groups of the \( \text{C}_{12}\text{E}_5 \) surfactant, which are oriented toward the inner part of the droplets, are capable of reducing Ag\(^+\) ions upon radiation. To check this hypothesis, Rivadulla et al. tried to obtain Pt by keeping samples at different temperatures with/without exposure to light irradiation but changing the system to AOT/\( n \)-hexane/water, because in this surfactant there are no terminal hydroxyl groups. Very small changes were observed at room temperature. At 50 °C the reaction produces a typical brown color, which appears after few minutes. The reactions are catalyzed by exposure to daylight, but the reaction is strongly dependent on the temperature due to the chemical reduction by the surfactant molecules. After 48 h at 50 °C the microemulsion shows a spectrum identical with that observed by Pt particles obtained by hydrazine reduction, confirming the formation of colloidal Pt particles without reductant addition. As the heads of the ionic surfactant AOT are composed of sulfonate groups, the reduction can be explained by assuming that the electronic pairs of the oxygens in the sulfonate group donate the electrons, causing reduction during irradiation, such as the oxygens of the hydroxyl groups of the \( \text{C}_{12}\text{E}_5 \) molecules. Colloidal Pt was obtained without hydrazine by heating and daylight exposure. The optical properties of the metallic particles are identical with properties of the corresponding particles prepared with hydrazine.

3.3. Cadmium nanoparticles

Demonstration of self-reproduction of sodium octanoate reversed micelles (in isooctane and octanol solvent mixtures) by the hydrogen-sulfite-mediated acid-catalyzed hydrolysis of octyl octanoate (OOL) is the significance of the present work [68]. OOL underwent hydrolysis in sodium octanoate (NaOA) reversed micelles, containing \( W = [\text{water}]/[\text{NaOA}] = 40 \). The products of the hydrolysis, octanoic acid (OA) and octanol (OL), lead to the formation of additional
reversed micelles; hence the process is considered to be self-reproducing. Self-reproduction was found to be catalyzed by lithium hydroxide, solubilized in the water pools, as well as by hydrogen sulfide, added to the solution of the reversed micelles. Addition of hydrogen sulfide to cadmium perchlorate containing self-reproducing reversed micelles resulted in the formation of optically transparent cadmium sulfide (CdS) nanoparticle dispersions. Diameters of the CdS-containing nanoparticles could be altered from 5.4 to 1.8 nm by changing the [Cd$^{2+}$]/[H$_2$O] ratios from 0.25 to 10.

Observation of the decrease of the size of the reversed micelles provides, therefore, an evidence for self-reproduction. Hydrolysis of OOL in the environment of NaOA reversed micelles resulted in the formation of octanoic acid (HOA), and octanol. The products of the OOL hydrolysis are the micelle-forming surfactant (OA) and the cosurfactant (or cosolvent, OL) whose assembly into additional reversed micelles constitutes the self-reproduction. The OOL-mediated self-reproduction of reversed micelles was referred to the particle size ($r_p$—hydrodynamic radius) monitored by the light scattering measurements (Table 2).

Table 2

<table>
<thead>
<tr>
<th>[NaOA]$_i$ (M)</th>
<th>[LiOH]$_i$ (M)</th>
<th>[H$_2$S]$_i$ (M)</th>
<th>$r_p$,nom (nm)</th>
<th>$r_p$,nom (nm)</th>
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<td></td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.0025</td>
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<td>4.5</td>
<td>134</td>
</tr>
<tr>
<td>0.1</td>
<td>0.005</td>
<td>4.9</td>
<td>4.5</td>
<td>722</td>
</tr>
<tr>
<td>0.1</td>
<td>0.01</td>
<td>4.9</td>
<td>4.5</td>
<td>722</td>
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<tr>
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<td>3.9</td>
<td>336</td>
</tr>
<tr>
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<td>0.0002</td>
<td>4.8</td>
<td>3.9</td>
<td>288</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0001</td>
<td>4.8</td>
<td>3.8</td>
<td>288</td>
</tr>
</tbody>
</table>

*a* Hydrolysis of OOL in NaOA reversed micelles in 85:15 = IO:OL, containing $W$ = 40, at room temperature. The hydrolysis was initiated by the injection of 0.025 M octylcococtanoate into reversed micelles. All concentrations are stoichiometric with respect to the organic solvent mixture. The subscript $i$ denotes the initial state $t=0$ h, and eq the equilibrium at $t$ in hours (brackets).

...and H$_2$S) have been shown to control the sizes of the CdS particles formed [69].

The CdS nanoparticles formed were capped by mercaptopropionic acid, isolated as solids, and could be repeatedly redispersed in water without changing their sizes. The reversed micellar solution became cloudy immediately following the addition of 3-mercaptopropionic acid and ultimately a colored precipitate became observable. Capping is known to arrest the growth of the nanoparticles and to permit the isolation of capped nanoparticles. Furthermore, aqueous dispersions of the capped CdS nanoparticles could be repeatedly isolated (by rotary evaporation), dried and redispersed in water to give nanoparticles with the same absorption threshold.

CdS nanoparticles were immobilized directly on top alkanedithiol-modified zinc (Zn) doped silica particles, which were themselves prepared via hydrolysis of tetraethyloxyhtrosilicate in the presence of zinc nitrate (Zn(NO$_3$)$_2$) followed by contact with dithiol (dt) molecules [70]. The CdS nanoparticles were generated in the reverse AOT/water/isooctane microemulsion. The AOT/isooctane reverse micellar solution containing Cd(NO$_3$)$_2$ ($W$ = [water]/[AOT] = 4) was added rapidly to a second micellar solution of the same $W$, containing Na$_2$S. After the formation of CdS particles, dt–Zn–SiO$_2$ was added to the reverse micellar solution. The size of the Zn–SiO$_2$ primary particles was smaller than 1 µm but was aggregated. No remarkable change in the size and morphology was observed for the Zn–SiO$_2$ particles, following the surface modification of the particles with dithiol molecules. Zinc and sulfur were both found on the Zn–SiO$_2$ particles by the EDX analysis. The absorption spectra ($\lambda_{abs,max}$ = 420 nm) for CdS nanoparticles, prepared in reverse micellar solution disappears from the supernatant solution, consequent to the addition of ethanedithiol–Zn–SiO$_2$. This indicates that almost all the CdS nanoparticles in the reverse micellar solution are immobilized successfully onto the ethanedithiol–Zn–SiO$_2$ particles.

The diffuse reflectance spectra for CdS nanoparticles prepared at various $W$ values and immobilized on ethanedithiol–Zn–SiO$_2$ are shown in Fig. 3. The characteristic absorption for CdS nanoparticles is observed, and a quantum size effect is exhibited, as shown by the blue shift in the absorption onset, as compared with that for bulk (500 nm). The corresponding nanoparticle size, thus estimated, is 3.7 nm for $W$ = 2, 4.1 for $W$ = 4, 4.3 nm for $W$ = 6 and 5.1 nm for $W$ = 8. No red shift in the absorption onset wavelength was observed during the course of immobilization, indicating that the size of the nanoparticles is retained.

The resulting CdS–Zn–SiO$_2$ composite was then used as a photocatalyst for the generation of Hz from 2-propanol aqueous solution. Under UV irradiation ($\lambda > 300$ nm), a high photocatalytic activity was observed for the CdS–Zn–SiO$_2$ composite material. This is effect-
ed by electron transfer from the photoexcited ZnS (dithiol-bonded Zn on SiO₂) to CdS nanoparticles. The photocatalytic activity is increased with a decrease in the number of methylene groups in the dithiol molecules, according to the rank order 1,10-decanedithiol < 1,6-hexanedithiol < 1,2-ethanediithiol.

The formation of semiconductor CdS nanoparticles via Cd emulsifier Langmuir–Blodgett (LB) films exposure to H₂S also resulted in generation of flatten CdS clusters [71]. The morphology of CdS particles was dependent on the LB film matrix. Thus, the generation of ultraflat CdS particles in calixarene LB films did not affect substantially their layered structure, in contrast cadmium stearate LB films were substantially destroyed by formation of much larger CdS clusters [72]. These results give evidence that the slowing down of the twodimensional nanoparticles growth rate results in the formation of more flatten nanoparticles.

CdS nanoparticles were prepared in reverse micellar systems (W=6) by mixing the same water/AOT/isooctane microemulsions, one containing (0.2 mM) cadmium nitrate (Cd(NO₃)) and the other (0.2 mM) Na₂S [73]. The commercial-grade alumina and silica particles were utilized as solid supports for CdS nanoparticles. The immobilization proceeded via simple addition of thiol-modified alumina or silica particles into reverse microemulsion containing CdS particles. The functionalization of the alumina and silica particles with a thiol group was carried out using a thiol-functionalized alkoxy-silane such as 3-mercaptopropyltrimethoxysilane (MPTMS) or 3-mercaptopropylmethyldimethoxysilane (MPDMS). The resulting thiol-modified particles are denoted as Al₂O₃–SH and SiO₂–SH. In the case of the addition of Al₂O₃–SH, the absorption corresponding to CdS nanoparticles (Fig. 4, curve 1) disappears from the supernatant solution (curve 3), whereas no change in the absorption spectrum is observed in the case of the addition of alumina particles without thiol modification (close to curve 1), indicating that the CdS nanoparticles are immobilized via chemical bonding between the thiol groups on the alumina particles and CdS nanoparticles.

The diffuse reflectance spectrum for the resulting Al₂O₃–CdS, measured in water dispersion, demonstrates the characteristic absorption of size-quantized CdS, as shown by curve (2) of Fig. 4. The immobilization of CdS particles of the size of 4.2 nm takes place.

The increase in W led to the increase in the CdS particle size:

\[ W/d \text{ (nm): } 2/3.9, 4/4.1, 6/4.2, 10/4.5 \]

The photoirradiation of CdS nanoparticles sometimes causes undesirable aggregation of the nanoparticles immobilized by the thiol-modified supports such as polystyrene particles [74]. When the CdS nanoparticles are immobilized by the SiO₂–SH particles, the absorption onset for CdS shifts toward the longer wavelength during photoirradiation in 10 vol.% 2-propanol aqueous solution, and indicating that the photo-induced growth of CdS nanoparticles occurs for SiO₂–CdS. In contrast, almost no change is seen in the diffuse reflectance spectrum for CdS immobilized by Al₂O₃–SH following 18 h of photoirradiation, which indicates Al₂O₃–CdS is more stable than SiO₂–CdS against irradiation and the CdS nanoparticles appear to retain their quantum size effect. Alumina supports are excellent in their thermal and chemical stability. Composite Al₂O₃–CdS particles are utilized as photocatalyst for H₂ generation from water in the presence of a sacrificial electron donor.

However, although the quaternary CTAB reverse micelles can be utilized as microreactors to obtain size controllable particles, the CdS nanoparticles prepared in this system usually exhibits defect emission and the photoluminescence efficiency is dramatically reduced due to the localized surface-trap states and dangle bonds.

Fig. 3. Diffuse reflectance spectra for CdS nanoparticles prepared at various W values and immobilized on ethanedithiol–Zn–SiO₂.

Fig. 4. Absorbance spectra for CdS nanoparticles in reverse micellar solution (water/AOT/isooctane) (W=6) following 24 h of stirring (1) without alumina particles, (1) with alumina particles (close to curve 1), and (3) with Al₂O₃–SH. (2) Diffuse reflectance spectrum for CdS nanoparticles immobilized on Al₂O₃–SH, measured following dispersion in water.
As the high surface-to-volume ratio of the nanoparticles [75]. Therefore, in order to eliminate defect emission, effective surface modification can be employed to diminish the local trap sites and, thus, significantly increase the quantum yield of the excitonic emission [76]. It was also expected to modify the nanoparticles without destroying the reverse micelles, otherwise the aggregation occurred.

Quaternary CTAB/n-hexanol/n-heptane/water reverse micelles were used as effective microreactors to prepare uniform and size controllable CdS nanoparticles by modulating W [77]. The composition of the four-component reverse micelles is defined by three parameters: W (the molar ratio between water and CTAB), P (the molar ratio between n-hexanol and CTAB) and [CTAB]. The reverse micelles were saturated with sodium sulfide aqueous solutions at certain W, P and [CTAB]. Cadmium nitrate reverse micelles were prepared in the same way. Equal amount of cadmium nitrate reverse micellar solution was added dropwise to that of sodium sulfite at room temperature with continuous stirring. From Fig. 5 it can be seen that with the increase in W value, the droplet size increases gradually and the size of nanoparticles increases simultaneously, but a little smaller than the droplet dimension at the same W value, which was contrary to the expected results [75]. Average size of the nanoparticles and droplets increased from approximately 4, 6 to 8 nm and 5.1, 6.9 and 8.6 nm, with increasing W from 5.0, 16.4 to 24.5, respectively.

The emission band at approximately 550 nm was observed which correlated to electron transition from the excited states to the surface localized trap states. Bandgap emission, which comes from excitonic recombination, blue shifts with decreasing particle size and it is the characteristic property of the quantum confinement. In order to get the excitonic emission and improve the luminescence behaviors, reflux treatment was carried out immediately by diluting reverse micelles of CdS nanoparticles with same reverse micelle but substituting reactant solution with water. The strong blue emission of the CdS nanoparticles treated by reflux increased and the defect emission disappeared. With the prolonged reflux time, red shift of the emission due to the growth of CdS nanoparticles was observed.

The proposed mechanism for obvious excitonic emission and luminescence enhancement is due to the improvement of modification and crystallization of the CdS nanoparticles, which were supposed to cause perfect surface status of CdS nanoparticles. The capping reagent of cosurfactant of n-hexanol around the surface of CdS nanoparticles was increased by reflux treatment. The water in the nanoparticles was removed, and the modification was compacted. Therefore, trap sites on the nanoparticles surface decreased and the crystallinity was also promoted, thus the fluorescence efficiency was dramatically improved.

3.4. Palladium nanoparticles

The intensive studies on the formation of nanoparticles were devoted to the reverse micelles and microemulsions composed of bis(N-octylethylenediamine) metal(II) complexes. These systems have characteristic features that the metal ions are highly condensed in the mesoscopic water pools and a variety of the morphologies of the aggregation system are dependent on the water content and the complex concentrations [78,79].

Palladium nanoparticles were obtained from a novel type reverse (w/o) microemulsion of bis(N-octylethylenediamine)palladium(II) chloride/water/chloroform ([Pd(oct-en)₂Cl₂]/water/chloroform) using NaBH₄ as a reducing agent [80]. Relatively uniform-sized particles were obtained from 0.025 or 0.05 mol kg⁻¹ [Pd(oct-en)₂Cl₂] in chloroform solution at [water]/[[Pd(oct-en)₂Cl₂] (W)=7.6. Under this condition, twice the moles of free oct-en ligands for the Pd complex were added to stabilize the reverse micelles. At W>20, the water/Pd(oct-en)₂Cl₂/chloroform microemulsions without cosurfactant were obtained. At W=50 the TEM picture showed an onset of the bicontinuous structure. At W<10, the structure of the aggregates is surely a droplet-type reverse micelle. In the system A (W=7.6, [oct-en]=0.2 mol kg⁻¹, [Pd(oct-en)₂Cl₂]=0.05 mol kg⁻¹), the palladium particles are relatively uniform-sized and the sizes are smaller (dₚ=4.2 nm). In the system B (W=50, [Pd(oct-en)₂Cl₂]=0.5 mol kg⁻¹), the spherical domains of the w/o microemulsions are still present even when the structures of larger domains are close to the bicontinuous phase at W=50 and at a larger palladium concentration. The size and its deviation are somewhat larger compared to those at W=7.6, where the water pool is a droplet type. It is coincided with a result that the metal particles become smaller at a lower original metal concentration [81]. In the pres-
ence of methanol, the shape of the palladium particles is significantly deformed from the spheres.

The water/Pd(oct-en)\textsubscript{2}]Cl\textsubscript{2}/chloroform system has two characteristic features. Firstly, the highly condensed palladium nanoparticles were obtained by using the novel type double-chain palladium complex. This result is attributed to the high concentrations of the palladium (II) ions in the water domains of the present aggregation systems. Secondly, the structures of the aggregates of the original palladium complex surfactants were directly reflected in the shapes of the palladium nanoparticles because of the palladium being located in the head group of the original metal complex surfactant. In the alkylethylenediamine system, the palladium complex surfactant acts as both a metal ion provider and a metal-particle stabilizer, which is a rare case. As the alkylethylenediamine has a capacity to form metal complexes with various transition metals, this method will be universally applicable to obtain metal nanoparticles in high yield.

3.5. Silver nanoparticles

Metallic silver, either in bulk form or finely dispersed, is an increasingly important material in many technologies. It displays unique properties normally associated with the noble metals (chemical stability, excellent electrical conductivity, catalytic activity, etc.), along with other more specific ones (antibacteriostatic effects, nonlinear optical behavior, etc.), while still being reasonably priced. Consequently, highly dispersed silver nanoparticles are used as catalysts, as staining pigments for glasses and ceramics, as antimicrobial materials, in surface-enhanced Raman spectroscopy, as transparent conductive coatings, in electronics, etc.

Several methods were used in the past to prepare silver nanoparticles, including chemical reduction of silver ions in aqueous solutions with or without stabilizing agents [82], thermal decomposition in organic solvents [83], chemical and photoreduction in inverse micelles [84], and radiation chemical reduction [85]. However, most—if not all—procedures described so far yield stable silver dispersions only at relatively low concentrations of metal and, therefore, are not suitable for large-scale manufacturing.

Dodecanethiol-capped silver ‘quantum dot’ particles (Q-particles) have been synthesized using a novel biphasic microemulsion (Winsor II) [86]. The microemulsion consists of diethyl ether/AOT/water along with dodecanethiol, where dispersed microdroplets of water domains in organic bulk phase are in equilibrium with excess water. AOT as the anionic surfactant due to its higher solubility in organic phase helps to extract metal cations from the aqueous to reverse micellar phase. The metal ions concentrated in the dynamic reverse microdroplets were reduced with sodium borohydride and consequently capped by dodecanethiol particles present in the system.

FT-IR investigations and elemental analyses support the encapsulation of silver particles by dodecanethiol (DT) while the transmission electron micrograph reveals an average size of 11 nm. A comparison of the FT-IR spectra between 400 and 450 cm\textsuperscript{-1} of DT and encapsulated particles shows all the important bands of pure DT are clearly seen in the encapsulated particles. The similarity of the features confirms (i) the presence of thiol as an essential component of the composite nanoparticles and (ii) that the thiol molecule is not leached out during several washings of the precipitate. The ratio of the sum of the percentage of C, H, S and metallic content reveals that 3.5 silver atoms associate with four alkanethiol molecules.

The signals of the X-ray photoelectron spectroscopy (XPS) spectra acknowledge the presence of Ag and S in the synthesized composite particles. A high-resolution scan over the range 360–380 eV reveals a doublet of the Ag 3d\textsubscript{5/2} peak at 368.4 eV and the Ag 3d\textsubscript{3/2} peak at 374.4 eV, corresponding to a peak to peak separation of 6 eV due to the presence of the Ag\textsuperscript{0} state since the peak position, line shapes, and peak to peak distance of the silver doublet are standard measures of the silver oxidation state (Table 3). The standard binding energies for the Ag doublet (3d\textsubscript{5/2} and 3d\textsubscript{3/2}) are 367.9 and 374.9 eV, i.e. the separation of the peaks is 7 eV [87]. The sulfur region exhibits a broad S 2p peak at 162.6 eV. This core level is shifted by nearly 1 eV to lower binding energy from the position expected for an undisturbed S–H bond in thiol. The absence of peak at nearly 532 eV indicates formation of neither silver oxide (AgO, Ag\textsubscript{2}O) nor adsorbed oxygen on the surface.

Fig. 6 shows the thermogravimetric and differential thermal analysis of the silver nanoparticles. Apart from the initial slow change in weight, the TG curve exhibits a sharp weight loss in the range 270–320 °C. Since the boiling point of dodecanethiol is in the range 266–283 °C, the above weight loss can be possible due to the loss of thiol molecules [88]. The extension of stability of capped molecules (decomposition temperature 320 °C) further confirms the Ag\textsuperscript{0}–S bond formation during the preparation stage. Further evidence for this comes from the observed higher rate of weight loss covering a large temperature range (approx. 50 °C). The total

| Table 3 |
|-----------------|-----------------|-----------------|
|                | Sulfur (2p\textsubscript{3/2}), eV | Silver (3d\textsubscript{5/2}, 3d\textsubscript{3/2}), eV |
| Free thiol, C\textsubscript{13}H\textsubscript{26}S | 163.6 | 367.9, 374.4 |
| Metallic silver |                |                 |
| Capped particles| 162.6           | 368.4, 374.4    |

| \( S\textsubscript{2p}\textsuperscript{2} \) | \( S\textsubscript{2p}\textsuperscript{1} \) |
|-----------------|-----------------|-----------------|
| Capped particles | 162.6           | 368.4, 374.4    |

\( 238\text{eV} \) is shifted by nearly 1 eV to lower binding energy from the position expected for an undisturbed S–H bond in thiol. The absence of peak at nearly 532 eV indicates formation of neither silver oxide (AgO, Ag\textsubscript{2}O) nor adsorbed oxygen on the surface.
particles formed by the reaction of NaBH₄ CN dissolved in the reduction of silver and formation of silver nanoparticles. liquid membrane of the microdroplet, effectively causing the reducing agent apparently can penetrate through the material. After that, the absorbance of the 400-nm peak increased very rapidly and disturbance of the optic system. The injection of the reducing agent caused a temporary plasmon resonance absorption, centered at 400 nm with its characteristic peak, originated from the surface of the Ag nanoparticles. Approximately 4 nm in diameter are yellow in color due to the larger decomposition range of thiol molecules. The additional broad exothermic curve may be due to the larger decomposition range of thiol molecules.

Perfluorodecanethiol was reported to effectively stabilize silver particles in the supercritical CO₂ dispersion [89]. Nanometer-sized silver metal particles are synthesized by chemical reduction of Ag⁺ ions dissolved in the water core of water in supercritical fluid carbon dioxide (CO₂) microemulsion [90]. The surfactant system consisted of a mixture of AOT and perfluoroalkylpolyether phosphate (PFPEP) at W = [water]/[AOT] = 12. PFPEP serves as a cosurfactant to make the microemulsion soluble in CO₂ (AOT is not soluble in CO₂) [91].

Fig. 7 shows the UV–vis spectra of the silver nanoparticles formed by the reaction of NaBH₄ CN dissolved in CO₂ with Ag⁺ (AgNO₃) in the water core of the microdroplets [90]. Silver nanoparticles with sizes approximately 4 nm in diameter are yellow in color with its characteristic peak, originated from the surface plasmon resonance absorption, centered at 400 nm [91]. The injection of the reducing agent caused a temporary disturbance of the optic system. After that, the absorbance of the 400-nm peak increased very rapidly and reached a saturation value after approximately 25 s. The reducing agent apparently can penetrate through the liquid membrane of the microdroplet, effectively causing reduction of silver and formation of silver nanoparticles.

The formation of silver nanoparticles with NaBH₄ was also observed, but the intensity of the 400-nm absorption peak was much lower than that observed for the case of NaBH₃CN. The low solubility of NaBH₄ was probably a major factor limiting its use as an effective reducing agent for studying redox reactions in supercritical CO₂. The solubility of NaBH₄ in CO₂ is very small (<10⁻⁴ M in the presence of 5% ethanol). Furthermore, some precipitate was found in the injection vessel and in the reactor caused by the precipitation of the reducing agent during injection. When NaBH₃CN was used, no precipitation was observed.

Ag nanoparticles were generated in the microemulsion using N,N',N'-tetramethyl-p-phenylenediamine (TMPD) as the reducing agent [90]. The strong absorbance of TMPD in supercritical CO₂ with peaks approximately 563 and 607 nm appeared immediately after the injection, indicating that a redox reaction involving TMPD was occurring very rapidly in the system. The absorption peak of Ag nanoparticles approximately 400 nm was masked initially by the huge background absorption of the TMPD but became visible after approximately 50 s. The distribution of the size of the Ag nanoparticles using TMPD or NaBH₃CN as a reducing agent is about the same. Thus, the mechanism of the formation of Ag particles in CO₂/TMPD microemulsion is as follows: First, TMPD diffused from the fluid phase into the microemulsion, followed by the reduction of Ag⁺ to elemental Ag⁰ with the formation of TMPD⁺. The TMPD⁺ migrated from the water core to the supercritical CO₂ phase and underwent decomposition, as indicated by the rapid decrease of its absorption intensity. The absorption of Ag nanoparticles at 400 nm began to increase after the absorption was reduced to the near background level in approximately 50 s. The presence of TMPD⁺ probably would cause hindrance to the formation of Ag particles in the water core. Therefore, aggregation of the elemental Ag to form silver nanoparticles exhibiting characteristic surface plasmon resonance absorption at 400 nm.

Fig. 7. UV–vis spectra of the Ag nanoparticles prepared by reacting NaBH₃CN with silver nitrate in the water-in-supercritical-CO₂ microemulsion. (1) before the injection of NaBH₃CN, (2) after the injection of NaBH₃CN.
was delayed until TMPD\(^+\) was nearly depleted in the water core. After that, the intensity of the 400-nm peak continued to increase and reached a saturation value after 200 s. The redox reaction between Ag\(^+\) ion and the reducing agent appears to involve several processes, including the diffusion of the reducing agent from the fluid phase to the water core, redox reaction occurring in the water core, and distribution of oxidized form of the reducing agent between the water pool and the fluid phase. An important observation is that the rate of formation of Ag nanoparticles using TMPD (time for reaching the saturation value of the absorption intensity of the 400-nm peak) appears slower than that observed in the case of NaBH\(_4\):  

Time/the reducing agent: 25 s/NaBH\(_4\)CN < 200 s/TMPD < – /NaBH\(_4\) (the precipitation and low absorption of final Ag nanoparticles)  

Since oxidized products of NaBH\(_4\)CN are much smaller compared with TMPD\(^+\), it probably would diffuse faster and also would not create a steric hindrance for the formation of Ag nanoparticles in the water core.

A new reducing agent (quercetin, Qr) for the synthesis of Ag nanoparticles in reverse micelles was reported to generate highly stable and rather monodisperse particles [92]. The reducing agent of new type, namely, quercetin (Qr), one of the natural plant pigments (the group of flavonoids) was used. The authors found that apart from its strong interaction with performed nanoparticles, Qr reduces silver ions from aqueous salt solutions, presumably through the formation of an intermediate complex where electron density is shifted towards the silver ion. Further studies showed that the reduction reaction in reverse micelles in the formation of silver particles with optical absorption spectra strongly resembling those of typical silver nanoparticles synthesized in aqueous solution or in reverse micelles. Stable silver nanoparticles were obtained in the presence of air oxygen in water/AOT/n-alkane system by the reduction of silver salts with Qr. Particle formation in the presence of Qr in micellar solution was detected by characteristic changes of optical absorption spectra after addition of AgNO\(_3\) as water solutions. Addition of the aqueous silver salt solutions to the micellar solutions of Qr resulted in the appearance of intensive coloration, red-brown. One can observe the appearance of new absorption band \(\lambda_{\text{max}} = 400-410\) nm for silver nanoparticles. Furthermore, the particle band grows, for example, with Qr concentration and time (for the silver particles, \(C_{\text{Ag}} = 3\) mM, \(W = 3.7\)):  

\[
\text{O.D.} /[\text{Qr}] / \mu \text{M}: 0.45/42, 0.8/115, 1.2/142
\]

\[
\text{O.D.} / \text{time (min)}: 0.39/5, 0.48/25, 0.54/60, 0.58/120 \text{ day}
\]

The theoretical curves (the Mie theory) lie much higher than the experimental one; it means that not all silver ions present in the system participate in the particle formation. Furthermore, the curves calculated for \(C_{\text{AgNO}_3} = 1.75\) and 1.85 mM fit the experiment in the short-wave range; at \(\lambda > 420\) nm the measured absorbance is higher than that predicted by the theory. To the first approximation, this result may be interpreted as showing that only 60% of the ions participate in particle formation. The increase of absorbance at the long-wave side was connected with the interaction of particle surface with the surrounding medium (e.g. with the headgroups of surfactant) [93]. Alternatively, it may result from the interaction of particles, which is disregarded in the Mie theory. For silver hydrosols, the appearance of a long-wave wing in absorption spectrum may be caused by the formation of the aggregates of silver (so-called fractal clusters) [94].

Barwick et al. [95] have synthesized Ag colloids in \(C_{12}E_5\)/cyclohexane/water microemulsions by using daylight irradiation of the AgNO\(_3\) dissolved in the dispersed aqueous phase. Authors explained their results, assuming that the terminal hydroxyl groups of the \(C_{12}E_5\) surfactant, which are oriented toward the inner part of the droplets, are capable of reducing Ag\(^+\) ions upon radiation.

The precipitation process yields highly concentrated and stable dispersions of monodisperse silver nanoparticles in a simple manner, by reduction of concentrated aqueous solutions of silver nitrate with ascorbic acid in aqueous medium [96]. Stable Ag particles of narrow size distribution were prepared by reducing silver nitrate in the presence of Daxad 19 (sodium salt of a high-molecular weight naphthalene sulfonate formaldehyde condensate) as stabilizing agent. Other emulsifiers, such as Tween 20, SDS, CTBA (cetyltrimethylammonium bromide), polyoxyethylene non-ylphenyl ether (Igepal CO-630) and alkyl ether sulfonate were ineffective for the preparation of stable Ag particles.

The absorbance \(A\) spectra indicate that during the very early stages \((\leq 1\) min) the number of silver particles increases (5 wt.% Daxad 19, 0.3 mol dm\(^{-3}\) AgNO\(_3\), 0.25 mol dm\(^{-3}\) ascorbic acid):  

\[
A / \text{time (s)}: 0.95/15 \text{ s, 1.55/30 s, 2.0/60 s}
\]

The precipitation of nanosized silver particles starts almost immediately on addition of the reducing agent, and continuous throughout the investigated period, that is, the intensity of the plasmon band at 413 nm increases with the reaction time. The particle size \((d_p/\text{nm})\) increases with the reaction time \((t)\):  

\[
d_p (\text{nm}) / t (\text{min}): 15 \text{ nm/1 min, 26 nm/7 min (the end of reaction)}
\]

Increasing the concentration of Daxad 19 increased stability of dispersion. The lowering the amount of this stabilizer resulted in aggregated dispersions. However, a rather unexpected finding that the lowering of the initial
concentration of AgNO₃ leads to larger particles and less stable silver hydrogels. One aspect that could account for the observed behavior is the interaction between the Ag⁺ ions and the sulfonic group of the Daxad 19 to form a silver/dispersant complex, which may act as a more effective protective species in this system. The decrease in the initial concentration of Ag⁺ would result in a lower concentration of this active dispersant and, therefore, weaken the particle protection. This stabilization mechanism could also explain the agglomeration of the silver hydrosol, when the concentration of the Ag-emulsifier complex decreases due to the reduction of silver ions to metallic atoms.

Ascorbic acid was selected as the reductant of choice, because of its ability to precipitate metallic silver in acidic solution according to:

\[ 2\text{Ag}^+ + \text{C}_6\text{H}_5\text{O}_6 \rightleftharpoons 2\text{Ag}^0 + \text{C}_6\text{H}_5\text{O}_6 + 2\text{H}^+ \]

The important aspect of this process is the increase in the acidity of the reaction mixture during the reduction, due to the release of protons. Most of other common reducing agents, such as hydrazine and formaldehyde, are effective only in solutions of neutral or basic pH and, therefore, require a base to complete the reaction.

It is known that \( E^0 \), the standard redox potential of reactions that involve \( \text{H}^+ \) and \( \text{OH}^- \) ions, is highly dependent on the pH. The changes in the redox potential of the reducing species affect \( \Delta E^0 \) of the overall redox reaction, causing changes in the supersaturation concentration of metal atoms and, consequently, the nucleation rate, which control the final particle size. In the case of ascorbic/dihydroxyascorbic system, an increase in the concentration of protons reduces the ability of the oxidized species to supply electrons, causing a significant slowdown of the reduction reaction. To verify these assumptions, the pH of the silver nitrate solutions was lowered by the addition of HClO₄, an acid that does not form any complexes or compounds with the Ag⁺ ions; thus, it affects the redox potential of only ascorbic acid, but not of the Ag⁺/Ag⁰ system. As predicted, starting from a silver nitrate solution acidified with perchloric acid the reduction reaction was slower and the size of the final individual silver particles was significantly larger (\( d = 80 \text{ nm} \)). However, stable hydrosols of nanosize silver particles were not obtained at the early stages of precipitation, since at the low pH of the reaction medium the particle charge was weaker, lowering the stability of the dispersions.

It was also observed that the majority of the Ag particles in this case exhibit internal structure, characterized by strain effects and/or stacking faults that can be related to ‘multi-twinned particle’ (MTP) formation [97]. The silver/silica core shell particles (Ag-doped silica colloids) are prepared by photoreduction of silver nitrate using visible laser irradiation [98]. The colloidal silica particles are discrete uniform spheres of silica with 22 nm average diameter and their surface is negatively charged due to the presence of \( >\text{Si}–\text{O}^- \) groups (at pH \( \approx 9.0 \)). Because of the electric charge, the particles repel one another, resulting in a stable product. The stability increases with dilution and decreases with temperature, resulting in gelation or aggregate formation. After addition of silver nitrate, silver ions could adsorb on silica [99], but in alkaline medium they are hydrolyzed to AgOH, giving rise to a surface complexation mechanism such as:

\[ >\text{Si}–\text{OH} + \text{AgOH} \rightarrow >\text{Si}–\text{OAg} + \text{H}_2\text{O} \text{ or } >\text{Si}–\text{O}^- + \text{AgOH} \rightarrow >\text{Si}–\text{OAg} + \text{OH}^- . \]

Then, photoreduction occurs by irradiation with visible light and silver nanoclusters are obtained at the surface of the colloidal silica, seen by the occurrence of a surface plasmon resonance at approximately 410 nm (Fig. 8), similar to that observed in pure silver hydrosols [100]. During the photoreduction process of the silver ions, an absorption broad band progressively increases with the irradiation time. This band, which is not present in the pure colloidal silica, is attributable to the surface plasmon absorption of metal nanoclusters, obtained by photoreduction onto the silica particles (Fig. 8). Silver particles with \( d \) ca. 20–30 nm are formed onto the silica particles, but with a significant amount of larger aggregates, also indicated by the broad tail of the plasmon resonance band in the visible region.

A strong SERS effect is found for colloids irradiated by laser lines in the 457.9–514.5 nm region, whereas the colloid irradiated by yellow light (568.2 nm) shows a negligible Raman enhancement. In order to evaluate the enhancement factors, the SERS intensities are compared with the weak Raman intensity observed in the colloid irradiated by the 647.1 nm line, without photoreduction of silver nitrate. For the colloid irradiated with...
the 514.5 nm laser line the relative enhancement factor, with respect to the colloid without silver particles, is found larger by two size orders (approx. 1.1 × 10^5). This agrees with enhancement factors usually detected in pure silver hydrosols [101] compared to the aqueous solutions containing the same ligand concentrations. In the case of colloidal silica, a fluorescence band occurs with maximum at approximately 480 nm. After photo-reduction of silver ions, a drastic quenching of the fluorescence is observed in Ag-doped silica colloids along with a shift of the peak to 495 nm. This evidence can be interpreted on the basis of the formation of a non-fluorescent complex between the fluorophore and the quencher [102], i.e. the silver clusters obtained by photoreduction onto the silica surface.

3.6. Copper nanoparticles

The reducing agent of new type, namely, quercetin (Qr), one of the natural plant pigments was also used to reduce Cu salts [92]. Stable copper nanoparticles were obtained in the presence of air oxygen in water/AOT/n-alkane system by the reduction of copper salts with Qr. Particle formation in the presence of Qr in micellar solution was detected by characteristic changes of optical absorption spectra after addition of Cu(NO₃)₂ as water solutions. Addition of the aqueous copper salts solutions to the micellar solutions of Qr resulted in the appearance of bright yellow for smaller and light brown for larger copper concentrations. A new absorption band appeared at λ_{max} = 425–440 nm for copper nanoparticles. The spectra copper nanoparticles in the AOT/water/Cu(NO₃)₂/Qr were shifted to shorter wavelengths (λ somewhat above 420 nm) [94] compared to those for copper nanoparticles stabilized by gelatin [103] and polyvinylpyrrolidone [104]. In the last two systems, λ_{max} was found to be 620–630 nm and 580–582 nm.

Reduction by hydrazine from Cu(AOT)₃ surfactant in reverse micelles gives copper nanoparticles with λ_{max} = 566 nm [105]; the authors found also that for W=3, a strong absorption at 800 nm is registered, caused by the copper oxide formation. The difference in λ_{max} values was observed to vary with the copper salt. For example, in the case of copper nitrate (Cu(NO₃)₂) λ_{max} = 435 nm, while for the copper ammonium chloride (Cu(NH₃)₂Cl₂) λ_{max} = 545 nm, so it is observed the marked red shift of the particle absorption band, with the fall of its intensity. These two salts used for the particle formation differ in the state of copper ion introduced into the Qr/AOT/heptane system. Obviously, the reduction of copper ion to atom and subsequent formation of particles in these cases goes with different rates and results, most likely, in different surface structure of the particles, which, in its turn, may manifest itself in the different properties of the surface plasmon. Nanometer-sized copper metal particles were synthesized by chemical reduction of Cu²⁺ ions dissolved in the water core of a water in supercritical fluid carbon dioxide (CO₂sc) microemulsion [90]. TMPD and NaBH₄CN were used to prepare Cu nanoparticles. When NaBH₄CN was used as the reducing agent, the rate of formation of Cu nanoparticles was faster than that observed for the TMPD case. The formation of Cu nanoparticles was virtually completed after approximately 30 s. In the TMPD case, the Cu nanoparticles in the water pool started to increase in approximately 100 s.

A microemulsion approach was used to produce a typical high-Τs superconductor YBaCuO. For this purpose, a microemulsion (water/ethyl oleate/labrasol/isostearic plurio) containing Y(NO₃)₃·5H₂O, Ba(NO₃)₂ and Cu(NO₃)₂·(5/2)H₂O, was mixed with another microemulsion containing ammonium oxalate [49]. The product obtained was successively washed with heptane, acetone, and water, treated 24 h at 824 °C in air, slowly cooled, and then treated for 6 h at 450 °C in oxygen. The powders obtained which have an initial size of ≈30 nm show an increase in size to the heat treatment (final average size ≈100 nm). The powders obtained, which are mainly made up of the superconducting orthorhombic phase, show a Tₘ ≈ 80 K, measured SQUID magnetometry, which is smaller than the Tₘ for larger particles (Tₘ = 93 K).

Nanoparticles of CuS were formed by exposing the deposited LB films of copper stearate to the H₂S atmosphere [106]. Initially flat and homogeneous film of copper stearate was transformed into a corrugated layer after the particle formation reaction. Such behavior indicates the fact, that the whole layer is involved into the reorganization during the particle formation. Removal of the fatty acid molecules with chloroform washing results in the formation of flat homogeneous layer of aggregated particles. During the reaction, protons of H₂S molecules attach themselves to stearic molecule head groups, while Cu²⁺ ions bind to the sulfur:

\[ \text{[CH₃(CH₂)₁₀COOH]₂ Cu + H₂S} \rightarrow \text{CH₃(CH₂)₁₀COOH} + \text{CuS} \]

Growth of these particles is rather random process—centers of nucleation can be distributed in the film in not regular manner. Formation of the particles results in the complete disturbance of the layer. After the removal of the corrugated organic matrix the layer begins to be again flat and homogeneous, what can be explained taking into consideration small sizes of the particles.

3.7. Nickel nanoparticles

The nickel fine particles have been prepared by the reduction of nickel chloride with hydrazine in the (w/
Effect of microemulsion composition on average diameter of nickel nanoparticles [103]a

<table>
<thead>
<tr>
<th>Water/CTAB/n-hexanol (wt.%)</th>
<th>CTAB/water (wt.%/wt.%)</th>
<th>CTAB/n-hexanol (wt.%/wt.%)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18/27/55</td>
<td>0.49</td>
<td>14.3</td>
<td></td>
</tr>
<tr>
<td>20/30/50</td>
<td>1.5</td>
<td>0.60</td>
<td>4.6</td>
</tr>
<tr>
<td>22/33/45</td>
<td>0.73</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>10/20/70</td>
<td>0.29</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>16/32/52</td>
<td>2.0</td>
<td>0.61</td>
<td>8.2</td>
</tr>
<tr>
<td>18/36/46</td>
<td>0.78</td>
<td>5.8</td>
<td></td>
</tr>
</tbody>
</table>

| a [NiCl₂] = 0.05 M. |

No significant reduction occurred at 25 °C even after several days, while the overall reaction including the reduction of nickel ions and the nucleation and growth of nickel nanoparticles was completed after 2 h at 40 °C and within 1 h above 70 °C. The selection of an appropriate reaction temperature and the addition of ammonia solution were two key points that the nickel nanoparticles could be prepared in the microemulsion system. The N₂ gas produced might auto-create an inert atmosphere, and hence the input of extra N₂ gas was not necessary. The average diameters of nickel nanoparticles decreased with the increase of water content at the weight ratios CTAB/water = 1.5 and 2 (Table 4). On the contrary, as expected, Nagy [108] found that the diameter of the microemulsion droplet (water/CTAB/n-hexanol) increased with the increase of water content due to the increase of the total volume of water and to the concomitant decrease of the total surface of the aggregate. Thus, the decreased diameter of nickel nanoparticles with the increase of the diameters of microemulsion droplets, was unexpected and seemed not consistent with the basic function microemulsion droplets to provide a limited volume for the formation of nanoparticles. Lufimpudio et al. [51] also observed similar phenomenon in the preparation of iron boride nanoparticles in the water/CTAB/n-hexanol system. Therefore, in addition to the size of microemulsion droplets, there must be other factors (e.g. the composition of microemulsion solution) affecting strongly the size of nickel nanoparticles formed in the water/CTAB/n-hexanol microemulsion.

The average diameter of nickel nanoparticles decreased with the increase of hydrazine concentration and approached to a constant value when the hydrazine concentration was above 0.5 M, i.e. [N₂H₄OH]/[NiCl₂] > 10 (Fig. 9).

Since a minimum number of atoms were required to form a stable nucleus, a collision between several atoms must occur for a nucleation. However, the probability was much lower than the probability for the collision between one atom and a nucleus already formed. That is, once the nuclei were formed, the growth process would be superior to the nucleation. In addition, the resultant nanoparticles were essentially monodispersed. Therefore, it might be suggested that all of the nuclei were formed almost at the same time and grew at the same rate. The number of the nuclei formed at the very beginning of the reduction determined the number and size of the resultant particles. At a low hydrazine concentration, the reduction rate of nickel chloride was slow and only few nuclei were formed at the early period of the reduction. The atoms formed at the later period were used mainly to the collision with the nuclei already formed instead of the formation of new nuclei and therefore led to the formation of larger particles. With the increase of hydrazine concentration, the enhanced reduction rate favored the generation of much more nuclei and the formation of smaller nanoparticles. When the concentration ratio of hydrazine to nickel was large enough (> 10), the reduction rate of nickel chloride was much faster than the nucleation rate and almost all nickel ions were reduced to atoms before the formation of nuclei. The nucleation rate was not further raised, and the number of nuclei held constant with the increase of hydrazine concentration.

![Fig. 9. Effect of hydrazine (■) and nickel chloride (□) concentration on the average diameter of nickel nanoparticles. Water/CTAB/n-hexanol = 22/33/45; 73 °C. (■): [NiCl₂] = 0.05 M, (□): [N₂H₄OH] = 1.0 M.](image)
As indicated in Fig. 9, it was found that the average diameter of nickel nanoparticles was not affected by the increase of nickel chloride concentration when the nickel chloride was below 0.1 M. The results revealed that the size of nickel nanoparticles was not affected significantly by the nickel concentration when the hydrazine concentration was large enough. When the concentration of nickel chloride was above 0.1 M, Fig. 9 showed that the average diameters of nickel nanoparticles increased significantly. This phenomenon could be explained by two possible reasons. One was that the hydrazine concentration was relatively lower ([Ni$_2$H$_2$OH]/[NiCl$_2$] < 10$^-7$) and led to the formation of fewer nuclei at the very beginning of the reduction. The other was that the number of atom formed at the very beginning of the reduction remained constant due to high ion concentration. The atoms formed at the latter period were used for the growth of particles and resulted in the formation of larger particles.

By analyses of electron diffraction pattern and X-ray diffraction (XRD), the resultant particles were characterized to be the pure nickel crystalline with a face-centered cubic (fcc) structure. The absence of possible oxides or hydroxide of nickel might be due to the fact that the reaction autocreated an inert atmosphere and was carried out at appropriate pH, temperature, and hydrazine concentration. Furthermore, the water confined in the microemulsion droplets usually has significantly lower activity than the bulk water because the average diameters of microemulsion droplets are very small. This might be another possible reason that no oxides or hydroxide were formed.

Nagy [108] reported that the average diameter of both the nickel boride and cobalt boride nanoparticles prepared in the (w/o) water/CTAB/n-hexanol microemulsion system decreased first and then increased with the increase of their corresponding metal salt concentrations. They considered that the formation of the relatively large particles at low ion concentration was due to the fact that only few water pools contained the minimum number of ions required to form a nucleus, and hence only few nuclei were formed at the very beginning of the reduction. When the ion concentration increased, they found that the number of nuclei obtained by reduction increased faster than the total number of ions, and hence the particle size decreased. When more than 80% of the water pools contained two or more ions, they suggested that the size of the resultant particles increased again due to the number of nuclei formed remained quasicontant with the increase of ion concentration.

The above discussed phenomena were inconsistent with the study by Chen and Wu [107], who referred them to the difference in the reduction, nucleation, and growth processes. The concentrations of ions and reducing agent affect the reduction rate and the distribution of ions (or atoms) in microemulsions. In addition to the collision energy and the sticking coefficient, the rates of both nucleation and growth are determined mainly by the probabilities of the collisions between several atoms, between one atom and a nucleus, and between two or more nuclei. The former kind of collision related to the nucleation, and the latter two kinds of collision refer to the growth process. The probability of the effective collision between one atom and a nucleus can be higher or smaller than those of the other two collisions. When the reduction was so large that almost all ions were reduced before the formation of nuclei, the number of nuclei formed was determined by the number of total atoms (ions), their distribution in microemulsions, and the collision energy and sticking coefficient for nucleation. (1) If the number of nuclei increased faster than that of total ions, smaller particles would be obtained. (2) If the increase of nucleus number was proportional to that of total ion number, the particle size might remained unchanged. (3) When the number of nuclei remained constant or increased slower than that of total ions, the particle size would become larger with the increase of ion concentration. The finding reported by Nagy at low ion concentration might belong to the first condition. The phenomenon observed by Nagy at high concentration and that observed by Lufimadio et al. [51] could refer to the third condition. For the Chen and Wu work, the effect of nickel chloride concentration on the size of nickel nanoparticles at a sufficient high hydrazine concentration might be described by the second condition.

The microemulsion procedure was used to prepare a great variety of Ni materials. For example, the (w/o) water/n-heptane/AOT microemulsion ($w = 10$) was used to prepare Ni particles by mixing of microemulsion containing NiCl$_2$ with another similar microemulsion containing NaBH$_4$ [49]. The X-ray diffraction of obtained powder (after the product was filtering, drying, and finally crystallized at 300 $^\circ$C) showing the main features of crystalline nickel. A (w/o) water/ethyl oleate/labrasol/isostearic plurol microemulsion containing FeCl$_3$ and NiCl$_2$ was mixed with another similar microemulsion containing NaBH$_4$ to obtain FeNi alloys. The particles were separated by ultracentrifugation and then washed with heptane and acetone. The magnetic properties of these samples measured in a magnetic field of Oe at room temperature (grain size ≈ 30 nm = droplet size) are: magnetization, $M = 4.2$ emu/g and coercive field, $H_c = 10$ Oe.

Synthesis of Ni-containing anisotropic flatten nanoparticles was carried out in a mixed Ni stearate/stearic acid and Ni arachidate/arachidic acid Langmuir–Blodgett (LB) films by borohydrid reduction under different reaction conditions [109]. Fig. 10 shows the compression isotherm of stearic acid (SA) monolayer on the aqueous subphase with 2 × 10$^{-4}$ M$^{-1}$ nickel acetate as a function
of subphase pH value. The characteristic phase transition in SA Langmuir monolayer on a pure water subphase at pH 6 and 21 °C takes place at 25 mN/m (Curve 1 on Fig. 10). Close compression isothersm are known for stearic (SA) and arachidic (AA) acid monolayers on the water subphase with multicovalent metal cations at low pH values when acidic carboxylic groups are protonated and metal cations do not bind and effect the monolayer [110]. Due to the metal cation binding with monolayer under increasing in subphase pH the fractions of free acid and soap coexist in monolayer what results in characteristic changes in monolayer compression isotherm due to phase behavior of a mixed monolayer [110]. At higher enough pH values dependent on the metal cation nature, the fatty acid monolayer is condensed and converted completely to the salt form. As it follows from curves 2 and 3 on Fig. 10 the fraction of Ni stearate soap in the monolayer increases with increase in pH value.

Three types of samples were prepared in the series of experiments—control multiplayer Ni-SA and Ni-AA LB films (sample 1), Ni-SA and Ni-AA LB films treated with diluted NaBH₄ solution (1×10⁻² M, pH 6.5) (sample 2), Ni-SA and Ni-AA LB films treated with concentrated NaBH₄ solution (1×10⁻¹ M, pH 10) (sample 3). In control sample 1 of Ni-SA LB film X-ray measurements indicate repeat distance d = 4.97 nm, corresponding to the structure period of Y-type divalent metal stearates LB film. Ordered lamellar structure of LB films was not disrupted noticeably by the nickel reduction procedure (samples 2 and 3). However, LB films with reduced Ni consists of two lamellar areas with different interlayer periods d₁ = 4.95 and d₂ = 4.1 nm. It implies that the generation of flatten Ni-containing nanoparticles can be an ordering factor, and also complete ionization of SA molecules in sample 3 can further improve the film structure. However, the formation of rather thick nanoparticles with the height (≈15–20 nm) exceeding the LB film bilayer structural unit, resulted in the disruption of LB film lamellar structure after the particle formation [111].

Fourier transform infrared (FTIR) measurements indicate that the fraction of protonated carboxylic groups in LB films is low probably due to the Ni²⁺ leaving LB films as a result of its chemical potential gradient. Infrared spectra obtained after the incubation of stearate LB film with NaBH₄ (0.01 M, pH 6.5) shows the increase in the transformation of Ni state salt molecules into protonated acidic form. After the treatment of the Ni stearate LB film with concentrated NaBH₄ (0.1 M, pH 10) all COOH groups were ionized. The film contain OH-coordinated to the metal ion or Ni hydroxide nanoparticles. Nanoparticles were directly observed by atomic force microscopy (AFM). The oblate shape of obtained nanoparticles can reflect the layered nature of LB film templates where important features are quasi-two-dimensional character of reaction area and mainly planar diffusion of active intermediates parallel to the surfactant layers resulting in the quasi-two-dimensional growth of flat nanoparticles. Mixed Ni soap/fatty acid LB films as precursors for nanoparticles synthesis and diluted with the reducing agent possibly resulted in the reduction of the nanoparticle growth rate with generation of rather flatten nanoparticles.

3.8. Gold nanoparticles

Depending on particle size, shape, and agglomeration, gold colloids can be red, violet, or blue. Gold colloids are furthermore used as electron-dense labeling agents in histochemistry and cytochemistry [7], and the high thermal and electrical conductivity of gold has led to its use in electronics [1]. Therefore nanosized gold nanoparticles stabilized within the polymer matrix might also be highly interesting for such applications. Finally, another important application for colloidal noble metals is in catalysis. Gold is often used in bimetallic-active systems to improve or modify the catalytic activity of catalysts such as palladium or platinum [1]. Gold nanoparticles have been reported to be useful as catalysts for the formation of hydrogen via transfer, storage and conversion of electrons into adsorbed hydrogen atoms [112]. They also show a high reactivity towards oxygen, a chemical property that results from size effects [113] which could offer new possibilities in oxidation catalysis.

Stable colloidal nanoparticles were prepared by the in situ reduction of tetrachloroauric acid (HAuCl₄) in the presence of protective polymers (Table 5) [114]. In the absence of any protective polymer, precipitation occurs immediately or shortly after the reduction under the conditions employed. Two in situ reduction methods are applied to the tetrachloroauric acid HAuCl₄ precursor,
namely photoreduction by UV irradiation and reduction by potassium borohydride. The reduction by potassium borohydride is an example of a fast reduction method performed at room temperature that should lead to small particle sizes. Usually, stable gold colloids with small particle diameters and no agglomeration are red. Any color change to violet or blue indicated starting agglomeration and subsequently, in many cases, particle precipitation.

Table 5 shows that in the presence of various protective polymers the slower reduction by UV irradiation usually results in larger particles. Examples are the colloids stabilized by poly(1-vinylpyrrolidone-co-acrylic acid) and by the poly(sulfonates). In contrast, the faster borohydride reduction method usually gives colloids that are stable for months with very small, spherical particles and narrower size distributions.

Table 5 shows that in the presence of various protective polymers the slower reduction by UV irradiation usually results in larger particles. Examples are the colloids stabilized by poly(1-vinylpyrrolidone-co-acrylic acid) and by the poly(sulfonates). In contrast, the faster borohydride reduction method usually gives colloids that are stable for months with very small, spherical particles and narrower size distributions.

The use of poly(sulfonic acids) resulted in very stable gold colloids, in fact stable for weeks or even months both from photoreduction and reduction by potassium borohydride. The negatively-charged poly(sulfonates), however, are less suitable stabilizers for gold colloids in comparison with the poly(sulfonic acids). Reasons for the poorer stabilization by the poly(sulfonates) might be the presence of sodium cations and the negative surface charge of the gold nanoparticles stemming from adsorbed chloride anions from the precursor. Advantage of good interactions with the gold precursor ion, here by complex or ion-pair formation after the protonation of the pyridine units, can also be seen from the results for the poly(vinylpyridines). For the poly(2-vinyl pyridine) the interaction is sterically hindered, which is not the case for the poly(4-vinyl pyridines). Consequently, the use of the poly(4-vinyl pyridines) results in more stable gold colloids with smaller particles. In the case of poly(4-vinylpyridine-co-styrene), additional stabilization is given through the more pronounced hydrophobic character of its polymer backbone. Polymer possessing a less hydrophobic backbone usually results in less stable colloids. This can be seen, for example, when comparing the results for the poly(2-ethyl-2-oxazolines) with the poly(ethylene oxides) of comparable molecular weights.

Relatively thick metallic gold nanoparticles were photo-chemically generated in multilayer LB films of positively charged amphiphiles deposited from an aqueous HAuCl₄ subphase (diameter ranged from 20 to 800 nm and height 15–20 nm, lamellar structure of LB films.

The water-cooled ethanolic solutions of [HAuCl₄] = 6.8 × 10⁻⁴ M containing the polymers in a mass ratio of polymer:gold 1:25 were irradiated. An aqueous solutions of KBH₄ was rapidly added to the stirred solutions (6.8 × 10⁻⁴ M) containing HAuCl₄ and the polymers in a mass ratio of polymer:gold 25:1, (1) reduced by KBH₄, (2) reduced by UV irradiation, Shoulder (weak, almost disappearing). Aggl.–agglomerates.

Table 5

Variation of the gold nanoparticle sizes with the type and molecular weight ($M_w$) of water-soluble polymers and random copolymers

<table>
<thead>
<tr>
<th>Polymer/mol. weight ($M_w$ × 10⁻⁴)</th>
<th>Color of colloid</th>
<th>UV–vis, $\lambda_{max}$ (nm)</th>
<th>$D$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
<td>(2)</td>
<td>(1)</td>
</tr>
<tr>
<td>Poly(2-ethyl-2-oxazoline)/2</td>
<td>Brownish-red</td>
<td>Shoulder</td>
<td>1.6</td>
</tr>
<tr>
<td>Poly(2-ethyl-2-oxazoline)/5</td>
<td>Brownish-red</td>
<td>Shoulder</td>
<td>1.3</td>
</tr>
<tr>
<td>Poly(ethyleneoxide)/2</td>
<td>Dark violet</td>
<td>Very broad</td>
<td>485–595</td>
</tr>
<tr>
<td>Poly(ethyleneoxide)/9</td>
<td>Dark purple</td>
<td>Shoulder</td>
<td>~540</td>
</tr>
<tr>
<td>Poly(2-vinylpyridine)/3</td>
<td>Purple</td>
<td>Shoulder</td>
<td>3.0</td>
</tr>
<tr>
<td>Poly(4-vinylpyridine)/3</td>
<td>Brownish-red</td>
<td>Shoulder</td>
<td>1.6</td>
</tr>
<tr>
<td>Poly(2-hydroxypropyl methacrylate)/2</td>
<td>Red</td>
<td>Very broad</td>
<td>3.7</td>
</tr>
<tr>
<td>Poly(styrene sulfonic acid)/2</td>
<td>Red</td>
<td>Broad</td>
<td>5.1</td>
</tr>
<tr>
<td>Poly(sodium-4-styrene sulfonate)/0.7</td>
<td>Violet/purple</td>
<td>Wine/Red</td>
<td>3.87</td>
</tr>
<tr>
<td>Poly(vinyl sulfonic acid, sodium salt)/0.05</td>
<td>Dark violet</td>
<td>Shoulder</td>
<td>7.6</td>
</tr>
<tr>
<td>Poly(2-acrylamido-2-methyl-1-propane sulfonic acid)/20</td>
<td>Red</td>
<td>Red</td>
<td>Broad</td>
</tr>
<tr>
<td>Poly(1-vinylpyrrolidone-co-vinyl acetate), 60/40 (mol.)/0.5</td>
<td>Violet</td>
<td>Purple/violet</td>
<td>75.9</td>
</tr>
<tr>
<td>Poly(1-vinylpyrrolidone-co-acrylic acid), 75:25 (wt.)/0.8</td>
<td>Brownish-red</td>
<td>Red/purple</td>
<td>38.6</td>
</tr>
<tr>
<td>Poly(4-vinylpyridine-co-styrene, 90:10 (wt.)/13.5</td>
<td>Brownish-red</td>
<td>–</td>
<td>Shoulder</td>
</tr>
<tr>
<td>Poly(dimethylamine-co-epichlorohydrin), 50:50 (mol.)/–</td>
<td>Orange-red</td>
<td>–</td>
<td>Shoulder</td>
</tr>
</tbody>
</table>

*The water-cooled ethanolic solutions of [HAuCl₄] = 6.8 × 10⁻⁴ M containing the polymers in a mass ratio of polymer:gold 1:25 were irradiated. An aqueous solutions of KBH₄ was rapidly added to the stirred solutions (6.8 × 10⁻⁴ M) containing HAuCl₄ and the polymers in a mass ratio of polymer:gold 25:1, (1) reduced by KBH₄, (2) reduced by UV irradiation, Shoulder (weak, almost disappearing). Aggl.–agglomerates.
was disrupted after the particle formation) [111]. Ligands containing thio, sulfide and amino functional groups that have good affinity for metal surfaces were used by Lin et al. to modify the surface of gold nanoparticles synthesized in a water-in-toluene microemulsion [115].

4. Conclusion

Microemulsion solutions are mostly transparent, isotropic liquid media with nanosized water droplets that are dispersed in a continuous oil phase and stabilized by surfactant molecules at the water/oil interface. These surfactant-covered water pools offer a unique microenvironment for the formation of nanoparticles. As a result, the particles obtained in such a medium are generally very fine and monodisperse. This is a new technique, which allows preparation of ultrafine metal particles within the size range 5 nm < particle diameter < 50 nm. The method of particle preparation consists in mixing of two microemulsions or microemulsion and aqueous solution carrying the appropriate reactants in order to obtain the desired particles. The interchange of the reactants takes place during the collisions of the water droplets in the microemulsions. This interchange of reactants is very fast, so that for the most commonly used microemulsions it occurs just during the mixing process. The reaction then takes place inside the droplets (nucleation and growth), which control the final size of the particles. The dynamic exchange of reactants such as metallic salts and reducing agents between droplets via the continuous oil phase is strongly depressed due to the restricted solubility of inorganic salts in the oil phase. The exchange of reactants can occur (1) by desorption of a reactant molecule out of the water pool, migration through the hydrocarbon phase and re-entry into a pool containing other reactant, or (2) by direct transfer between pools during the time of the collision between two droplets. The possibility of this process occurring would be enhanced in the case of the more energetic collisions and if collisions were strongly interactive. Generally the chemical reactions of reactants within the microdroplet is very fast and, therefore the rate-determining step in the overall reaction will be the initial communication step of the microdroplets with different reactants. The rate of communication has been defined by a second-order communication-controlled rate constant and represents the fastest possible rate constant for the system.

If the interaction is attractive, the duration of collisions increases, and transient clusters of droplets are formed. Interfaces overlapping occur during collisions, allowing exchanges between touching droplets. These exchanges are achieved by hopping of ions or molecules through the interfaces, or by transient opening of these interfaces with communication between the water cores of the droplets. This transfer can be achieved by charge hopping, or transient merging of connected droplets with communication between the water cores. The condition for proceeding of such events is that the droplet interactions are strongly attractive.

The concentrations of reactants affect the reduction rate and the distribution of ions (or atoms) in microemulsions. The rates of both nucleation and growth are determined mainly by the probabilities of the collisions between several atoms, between one atom and a nucleus, and between two or more nuclei. The former kind of collision related to the nucleation, and the latter two kinds of collision refer to the growth process. (1) If the number of nuclei increased faster than that of total ions, smaller particles would be obtained. (2) If the increase of nucleus number was proportional to that of total ion number, the particle size might remain unchanged. (3) When the number of nuclei remained constant or increased slower than that of total ions, the particle size would become larger with the increase of ion concentration.

Since a minimum number of atoms are required to form a stable nucleus, a collision between several atoms must occur for a nucleation. Once the nuclei were formed, the growth process would be superior to the nucleation. For the monodisperse particles, it might be suggested that all of the nuclei were formed almost at the same time and grew at the same rate. The number of the nuclei formed at the very beginning of the reduction determines the number and size of the resultant particles. The atoms formed at the later period are used mainly to the collision with the nuclei already formed instead of the formation of new nuclei and therefore lead to the formation of larger particles.

5. Nomenclature

\(a:\) polar head area of the emulsifier
\(A:\) absorbance
\(AA:\) arachidic acid
\(AFM:\) atomic force microscopy
\(AOT:\) bis(2-ethylhexyl)sulfosuccinate
\(CdS:\) cadmium sulfide
\(Cd(NO_3)_2:\) cadmium nitrate
\(CMC:\) critical micelle concentration
\(CTAB:\) cetyltrimethyl-ammonium bromide
\(Cu(NH_3)_2Cl_2:\) copper ammonium chloride
\(C_{12}E_{4}(\text{Brij 30}), C_{12}E_4, C_{12}E_6:\) poly(ethylene glycol)monododecyl ethers
\(Daxad 19:\) sodium salt of a high-molecular weight naphthalene sulfonate formaldehyde condensate
\(DLS:\) dynamic light scattering
\(DT:\) dodecanethiol
\(E^0:\) standard redox potential
\(fcc:\) face-centered cubic

\(\text{CdS}: \text{cadmium sulfide}\)
\(\text{Li}^+: \text{metallic salt}
\(\text{Li}^+: \text{metallic salt}
\(\text{NO}_3^-: \text{redox potential}\)
\(\text{Cl}: \text{copper ammonium chloride}\)
\(\text{Cl}: \text{copper ammonium chloride}\)
\(\text{Daxad 19}: \text{sodium salt of a high-molecular weight naphthalene sulfonate formaldehyde condensate}\)
\(\text{DLS}: \text{dynamic light scattering}\)
\(\text{DT}: \text{dodecanethiol}\)
\(\text{E}^0: \text{standard redox potential}\)
\(\text{fcc}: \text{face-centered cubic}\)
FTIR: Fourier transform infrared
HAuCl₄: tetrachloroauric acid
HLB: hydrophilic–lipophilic balance
HOA: octanoic acid
H₂PtCl₆: hexachloroplatinic acid
Igepal CO-630: polyoxymethylene nonylphenyl ether and alkyl ether sulfonate
kₖₒ₅: second-order communication-controlled rate constant
k₉: diffusion rate constant
l: fully extended chain length of the emulsifier.
LB film: Langmuir–Blodgett film
MPTMS: 3-mercaptopropyltrimethoxysilane
MPDMS: 3-mercaptopropylmethyldimethoxysilane
MTP: multi-twinned particle
NaBH₄: sodium borohydride
NaBH(OAc)₃: sodium borohydride octanoate
NaOA: sodium octanoate
OA: octanoic acid
OHIs: organic-inorganic hybrids
OL: octanol
OOL: octyl octanoate
[Pd(oct-en)₃]Cl₂: bis(N-octylethenediamine)palladium(II)
PFPEP: perfluoropolyether phosphate
RESS: rapid expansion of supercritical solution
SAXS: small-angle X-ray scattering
SA: stearic acid
SDS: sodium dodecyl sulfate
SERAs: surface enhanced Raman spectroscopy
TEM: transmission electron microscopy
TMPD: N,N,N',N'-tetramethyl-p-phenylenediamine
Tween 20: polyoxylethylene sorbitan monolaurate
V: emulsifier hydrocarbon volume
v/α·l: the packing parameter of emulsifier molecule in the micellar assembly
W: molar ratio of water and stabilizer (emulsifier) [water]/[stabilizer]
WI, WII, WII, WIV: Winsor I, Winsor II, Winsor III, Winsor IV
Zn(NO₃)₂: zinc nitrate
Q-particles: 'quantum dot' particles
Qr: quercetin
XPS: X-ray photoelectron spectroscopy
XRD: X-ray diffraction
φₑₑₑ: the percolation threshold

References

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