Review Article

Role of Surfactants in Nanotechnology and Their Applications

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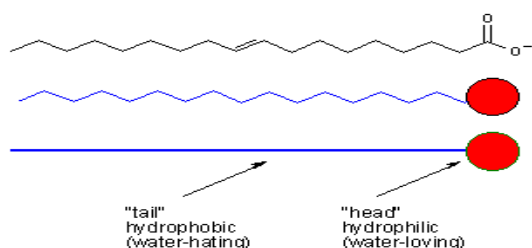*Corresponding author*

A B S T R A C T

Keywords

Nanoparticles;
nano-emulsions;
pharmacy ,
drugs,
agrochemicals
and cosmetics.

The Main goal of surfactants in the formation of nanoparticles is due to its high effect on the dispersion. Nano-emulsions, as non-equilibrium systems, present characteristics and properties which depend not only on composition but also on the preparation method. Although interest in nano-emulsions was developed since about 20 years ago, mainly for nanoparticle preparation, it is in the last years that direct applications of nano-emulsions in consumer products are being developed, mainly in pharmacy, drugs, personal care, health care, agrochemicals and cosmetics. These recent applications have made that studies on optimization methods for nano-emulsion preparation be a requirement. This review is focused on the most recent literature on developments of nano-emulsions as final application products and on the optimization of their preparation.

Introduction

Surfactants are characterized by the essential features that we saw in sodium oleate. A surfactant molecule has a hydrophilic (water-loving) head and a long hydrophobic (water-hating or oil-loving) tail. For this reason, we often describe surfactants is being amphiphilic molecules - they love everything.

"tail"
hydrophobic
(water-hating)

"head'
hydrophilic
(water-loving)

Surfactants can be categorized according to the charge present in the hydrophilic portion of the molecule (after dissociation in aqueous solution):

- o Anionic surfactants
- o Nonionic surfactants
- o Cationic surfactants
- o Amphoteric surfactants

Surfactants Play major roles in the formation of nano-emulsions: By lowering the interfacial tension, laplace pressure P (the difference in pressure between inside and outside the droplet) is reduced and hence the stress needed to break up a drop is reduced. Surfactants prevent coalescence of newly formed drops.

Addition of more surfactants creates a smaller efficiency and possibly diminishes recoalescence. A surfactant mixture that shows a reduction in surface tension compared with the individual components can be used . If possible, the surfactant is dissolved in the disperse phase rather than the continuous phase this often leads to smaller droplets.

Nano-emulsions are transparent or translucent systems mostly covering the size range 50-100 nm (Narajima, 1997). They were also referred to as mini-emulsion (El-Aasser, 1997). Unlike microemulsion(which require a high surfactant concentrations, usually in the region of 26% and higher), nanoemulsion are only kinetically stable.

Nano-emulsions are attractive for application in personal care and cosmetics as well as in health care due to the following advantages

The very small droplet size causes a large reduction in the gravity force and Brownian motion may be sufficient to overcome gravity. This means that no creaming or sedimentation occurs on storage.

The small droplets size also prevents their coalescence, since these droplets are non-deformable and hence surface fluctuations are prevented. In addition, the significant surfactant film thickness(relative to droplet radius) prevents any disruption of the liquid film between the droplets.

Nano-emulsions are suitable for efficient delivery of active ingredients through the skin. The large surface area of the emulsion system allows rapid penetration of actives.

Due to their small size,nanoemulsions can penetrate through the"rough" skin surface and this enhances penetration of actives.

The fluidity of the transparent nature of the system, as well as the absence of any thickeners may give them a pleasant aesthetic character and skin feel.

The small size of the droplets allows them to deposit uniformly on substrates-wetting, spreading and penetration may be also enhanced because of the low surface tension of the whole system and the low interfacial tension of the O/W droplets.
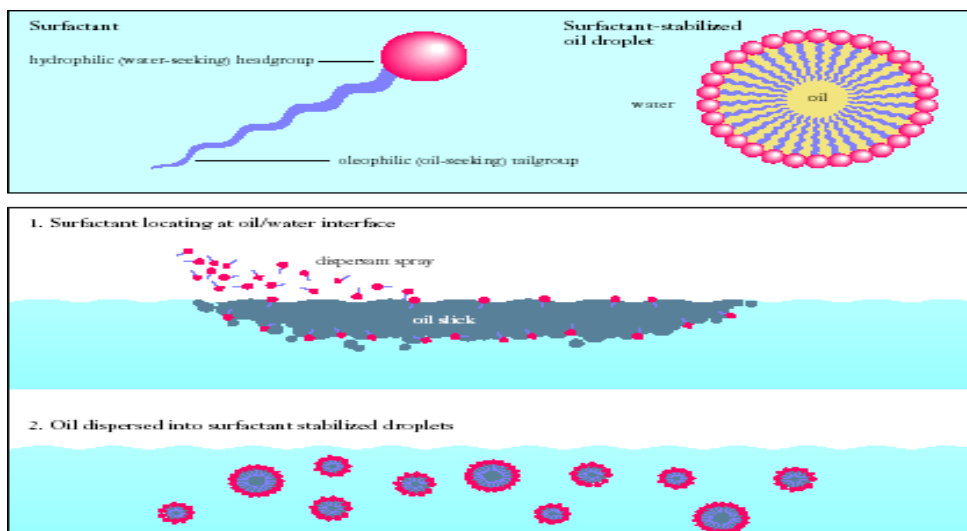
Nano-emulsions can be applied for delivery of fragrant, which may be incorporated in many personal care products. This could also be applied in perfumes, which are desireable to be formulated alcohol free.

Nano-emulsions may be applied as a substitute for liposomes and vesicles and it is possible in some cases to build lamellar liquid crystalline phases around the nano-emulsion droplets.
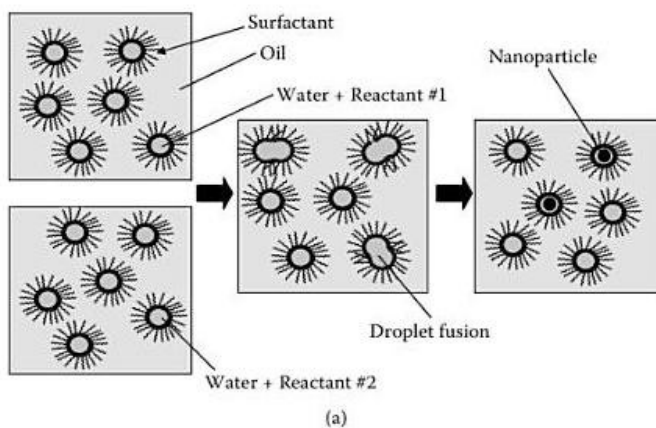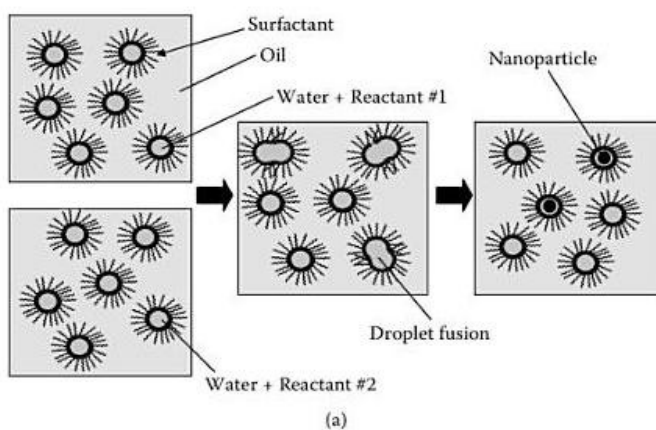
Despie the above advanags, nano-emulsions have only attracted interest in recent years because

Their preparation requires, in many cases, special application techniques such as the use of high-pressure homogenisers as well as ultrasonics has became available only in recent years.

There is a perception in the Personal Care and Cosmetic Industry that nano-emulsions are expensive to produce. Expensive equipment is required as well as the use of high concentrations of emulsifiers.

Figure.1(a) preparation of suspended nanoparticles by mixing two water-in-oil microemulsions. (b) Preparation of mixed platinum-palladium Nanoparticles.

(a)

(a)

Lack of understanding of the mechanism of the production of submicron droplets and the role of surfactants and cosurfactants.

Lack of understanding the interfacial chemistry involved in production of nano-emulsions.

However, despite these difficulties,several companies have introduced nano-emulsions in the market and, within the next few years, the benefits will be evaluated. Nano-emulsions have been used in the pharmaceutical field as drug delivery systems (Bentra S. and Levy, 1993).

There is a special and borderless science that deals with the nanostructural materials. These nanostructural materials are derived from nanoparticles. The uses of these nanostructural materials are immense and there are sufficient evidences that these nanoparticles display distinct characteristics from the microcrystalline structures. There is no scientific field where the nanomaterials are not being investigated and explored to find the advantages of these materials in improving the desired characteristics (Philip, 2001). Nanotechnology is somewhat of a 'catch-all' term used to describe a wide range of enabling technologies focused at the level of atoms and molecules, and is applicable to many different industry sectors. The design, production and application of structures at the 0.1–100 nm scale reaches across industries as diverse as the electronics, environmental, materials and healthcare sectors (Roco, 1999).
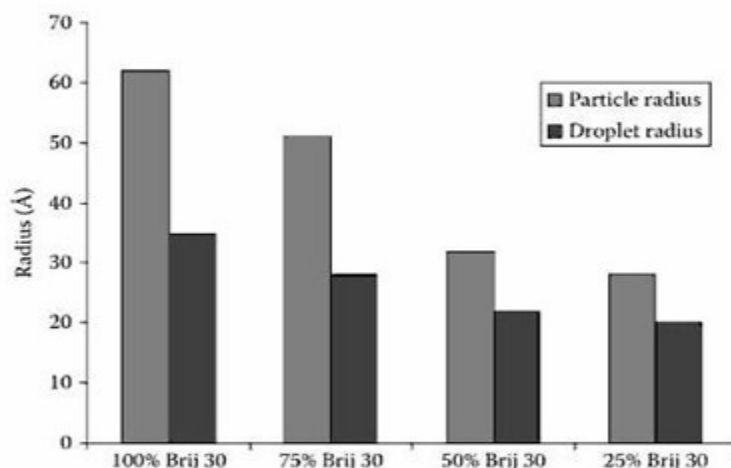
As biological systems interface with their surroundings through molecules and multi-molecular structures that operate at the nanoscale, it is easy to appreciate why nanotechnology has so much potential in healthcare, pharmaceuticals and biotechnology. Much of the cell's surface machinery and intracellular organelles operate at the nanolevel: regulating the actions of messenger molecules such as hormones and mediators; maintaining ionic stability; and manufacturing a wide variety of crucial building blocks for the body. Small nanosized molecules such as sugars and peptides (1–10 nm) 'dock' into larger nanosized molecules (10–100 nm) to mediate specific functions, or are processed further through the active sites of receptors or enzymes. Thus, the creation and control of matter in the form of molecular systems and devices at the nanometer scale through the integration of chemistry, physical sciences and molecular engineering, holds enormous promise for the future of medicine and healthcare (Roco, 1999).
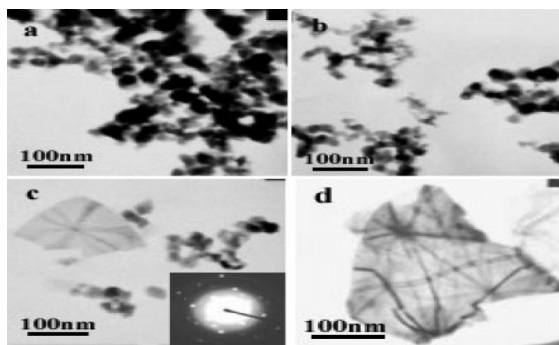
Nanoparticle synthesis is one of the complex processes. There are three main categories of nanoparticle synthesis and these are vapor phase, solution precipitation and solid-state processes. Although all the three are used for synthesis of nanoparticles the more common and widely used process is solid state. The solid-state process is also the cheapest process among all the three processes used for production of micron-sized particles(Philip, 2001).

In solid state synthesis of nanoparticles generally heat treatment followed by milling is carried out to get an average particle size of 100nm or less. Mechanical milling is one of the most preferred and earliest technique to produce metallic microcrystalline powder. People claims to get a nanoparticle of very small size of up to 30nm particle size by using media milling of very small size of 200 micro meter.
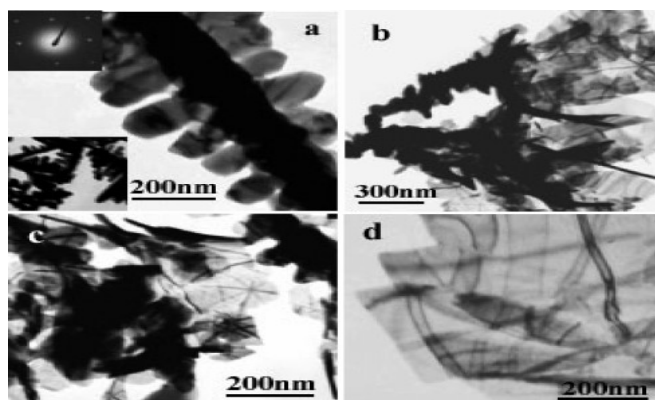
Figure.2 Microemulsion droplet radius and silver nanoparticle radius obtained by Reaction in microemulsion using different combinations (molar ratio Indicated) of the alcohol ethoxylate Brij 30 and the anionic surfactant AOT.

Figure.3 TEM images of (a) precursor and the samples prepared by hydrothermal treatment for (b) 45, (c) 60, and (d) 75 min. Reaction temperature: 160 □C. The inset in c is the SAED pattern of a single nanosheet.

Figure.4 TEM images of products synthesized with different amounts of SDBS: (a) 0.0, (b) 0.05, (c) 0.10, and (d) 0.15 g. The top inset in a is the SAED pattern, and the lower one is a low-resolution TEM imag

There are other commonly preferred milling methods used by different researchers includes dry milling and ball milling techniques (Philip, 2001).

In vapor-phase synthesis of nanoparticles, the formation of nanoparticles takes place in gas phase. In this synthesis technique the condensation of atoms and molecules is carried out. The vapor phase synthesis is not new and many multinational companies have been using flame reactors for decades for producing large quantities of nanoparticles. The flame reactors were used for forming various nanoparticles such as carbon black and titanium dioxide. The last and most advanced technique is known as inert gas condensation. Although the technique is costly, it is considered as a controlled process as by this method the exact shape and size of the nanoparticle can be synthesized. In inert gas condensation technique, the nanoparticle as soon as they formed rapidly collides with inert gas in a low-pressure environment and thus smaller and controlled nanoparticles are formed(Philip, 2001).

Synthesis of inorganic materials with nanosized dimensions can take advantage of the ability of surfactants to self-assemble into well-delined structures. These structures are used as a kind of template for the synthesis. This approach of nanomaterials preparation has triggered substantial interest both in the surface chemistry and the materials chemistry community. The accuracy and reproducibility of the self-assembly process has been seen as means of achieving control of materials architecture on the nanometer scale. This is a biomimctic approach: a wide variety of biological structural materials are made by a templating process with the use of surface active compounds (Holmberg et

al., 2002; Patarin et al., 2002; Palmqvist, 2003).

When nanoparticles are incorporated in compositions, a release of the active agents into the composition frequently takes place. In the particular case of nanocapsules, when they are incorporated in a composition containing an oily phase, such as for example emulsions, the active agents encapsulated in the oily core migrate to the oily phase of the composition. This premature release of the active agents into the composition makes their encapsulation in nanoparticles ineffective.

Preparation of Nanoparticles using Surfactants

The synthesis procedure for the preparation of metal nanoparticles from water-in –oil microemulsions is simple. Two microemulsions are formulated, one with a metal salt or a metal complex dissolved in the water pools and one with a reducing agent, such as sodium borohydride or hydrazine. The reaction leading to the solid materials, such as a reduction of a metal salt to the metal. The overall kinetics of the system are usually such that the particles cease to grow when they have reached a size comparable with the size of starting microemulsion. Thus, for systems involving fast reaction steps within the droplets, the overall reaction kinetics are mainly governed by transport of species through the hydrocarbon domain and by droplet fusion,which governs the size and the size distribution of the nanoparticles. The water droplets of the starting water –in-oil microemulsion should not be seen as a mold that is being filled with product during the course of the reaction. After completed reaction, a fine suspension of nanoparticles can be

obtained and this suspension coexists with a microemulsion consisting of water droplets in oil. The inorganic nanoparticles are most likely surrounded by a water film, and both the particles and the water droplets will be stabilized by a monolayer of surfactant. The surfactants will direct the polar head group into the water and the hydrophobic tails will be oriented into the continuous hydrocarbon domain. The process is illustrated in Figure (1.a) (Boutonnet et al., 1991).

Alternatively, one may mix three microemulsions, one containing a salt of the first metal, one containing a salt of the second metal, and one containing the reducing agent. As an example, mixed platinum-palladium nanoparticles in the size range of 5-40 nm can be prepared by mixing a nonionic surfactant-based microemulsion containing both platinum and palladium salts in the water pools with a hydrazine-containing microemulsion (Yashima et al., 2003). a bimetallic particle is shown in Figure (1.b).

Interestingly, Wu, Chen, and Huang (2001) found, in contrast, strong indications that their synthesis which was based on sodium bis (2-ethylhexyl) sulfosuccinate (AOT) as surfactant and hydrazine as reducing agent,resulted in Pt-Pd alloy particles. The reason for this difference is not clear, but the results indicate the importance of suitable surfactant-metal ion interactions for the formation of crystalline alloy nanoparticles in microemulsions.

The microemulsions of interest for the synthesis of inorganic nanoparticles are of water-in-oil type that is, they consist of small water droplets , surrounded by a monolayer of surfactants and dispersed in a continuous oil domain. Microemulsion
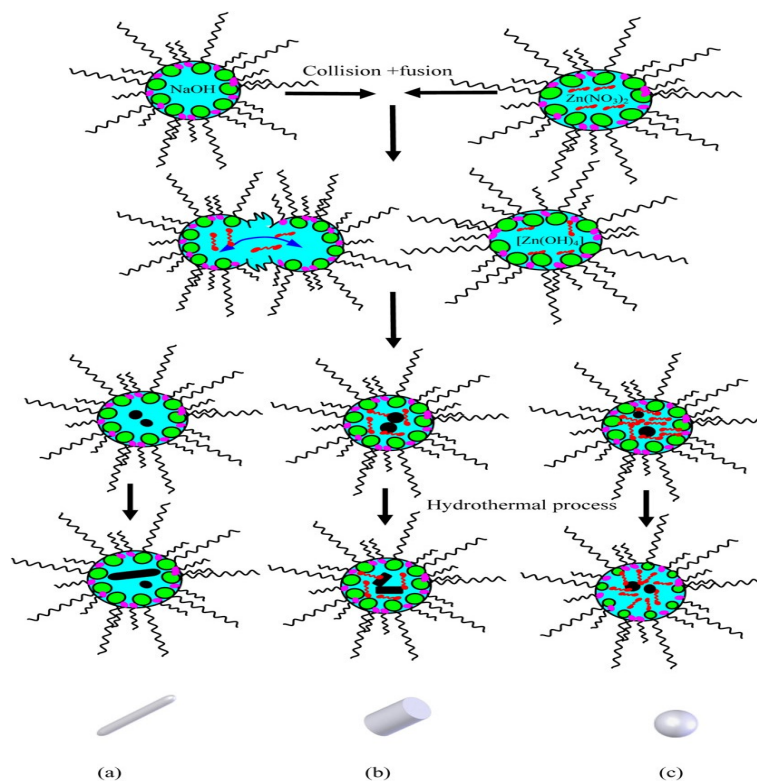
droplet radius and silver nanoparticle radius obtained by reaction in microemulsions using different combinations (Figure 2) of the alcohol ethoxylate Brij 30 and the anionic surfactant AOT. The results support that larger microemulsion droplets have a tendency to give larger particles and the study shows that the starting droplet size influences the size of the formed nanoparticles even though the actual sizes are different (Andersson et al., 2005).

The metal nanoparticles formed in the microemulsion-based synthesis are not always spherical. On preparation of copper nanoparticles from microemulsions with varying internal structures (Lisiecki et al., 2000; Pileni, 2001). Reaction in a microemulsion consisting of spherical water droplets gave spherical particles. Reaction in a microemulsion consisting of interconnected water cylinders yielded cylindrical copper nanocrystals (together with some spherical particles). Finally, reaction in a complex system consisting of a water –in-oil microemulsion coexisting with a lamellar phase gave a mixture of particles with different shapes: spheres,cylinders,flat objects,etc. An excellent example of this is again the formation of coppernanocrystals made from copper bis (2-ethylhexyl) sulfosuccinate (AOT) with sodium as counter ion exchanged by the divalent cuprous ion (Pileni, 2003; Filankembo A. and Pileni, 2000).
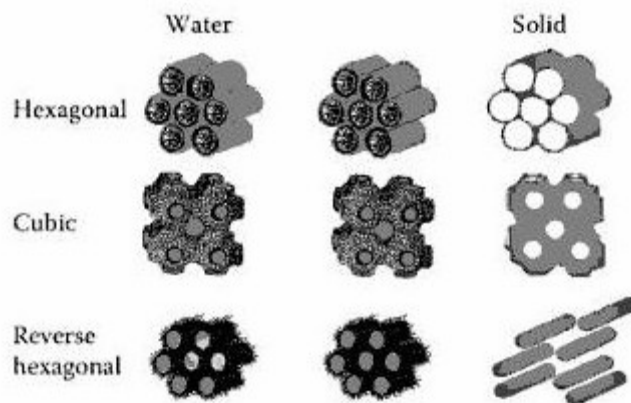
Yu and Kudo (2005) had synthesized bimetal (BiVO4) nanofibers with an average diameter of 100 nm and lengths of up to several micrometers by a surfactant-assisted hydrothermal synthesis using cetyltrimethylammonium bromide (CTAB), which proved to be an effective route to control the phase structure and

Figure.6 Synthesis and morphology control of crystalline ZnO particles in microemulsions. PEG400 concentration: (a) 0.0%, (b) 12.5% or 25.0%, (c) 50.0%.

Figure.7 Schematic illustration of how a surfactant liquid crystal is first solidified and then transformed into a mesoporous material by removal of the surfactant.Surfactant removal can be made either by washing or by calcinations.

morphology of the products. The hydrothermal process that generates high quality BiVO4 nanosheets is described. sodium dodecyl benzene sulfonate (SDBS) was used as the morphology-directing agent. As a typical soft chemical method, the hydrothermal process is promising for preparation of metal oxide nanosheets because of its many advantages. The method generates highly crystalline products, with high purity, narrow size distribution, and low aggregation. The morphology and crystal form of the products can be controlled by adjusting the hydrothermal reaction conditions (*Cushing, et al., 2002)(Fig 3 and 4)

To prepare the microemulsion (ME), a solution of heptane and hexanol was used as the oil phase and the polyoxyethylene tert-octylphenyl ether (Triton X- 100) was used as nonionic surfactant.

The growth mechanism of ZnO nanoparticles was proposed based on the restricting effect of microemulsions and the adsorption controlling effect of PEG400 molecules in the crystal growth process, as shown in Fig. 14. Needle-like ZnO with 150–200 in length were prepared by a microemulsion-mediated hydrothermal process without the addition of PEG400, which was due to the preferential growth of ZnO crystal growth along the direction. But the length of the needle-like samples is within 500 nm, which is smaller than those of ZnO nanobundles of about 1000 nm in length prepared using an aqueous solution precipitation method.

This phenomenon was attributed to the restricting effect of the microemulsion, and the surfactant and cosurfactant molecules present at the interface embraced the crystals and controlled their

excess growth (Li et al., 2009).

Using carboxylic acid (ACA) as the surfactant additive to inhibit ZnO nanoparticle growth both by coarsening and oriented aggregation as compared to using other monocarboxylates (e.g., acetate and tribromoacetate). (Ratkovich A.and Penn , 2009). The preparation of Ti1-xSnxO2 nanocrystalline in reverse microemulsions is reported. (Fresno et al., 2009). Platinum nanoparticles of less than 5 nm size have been synthesized by the reduction of H2PtCl6 using sodium borohydride in water-in-oil (w/o) microemulsions of water/TritonX 100/cyclohexene/1-hexanol at 25 ± 2 ∘C . The core–shell type Fe_3O_4 nanoparticles in poly(organosilsesquioxane) (Fe_3O_4) were prepared by one-pot synthesis using reverse micelle method. The confinement of finite amounts of nickel chloride in the hydrophilic core of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles dispersed in n-heptane has been investigated. Some reverse micelle-based template methods are availabl to control the copper particle size.Reverse micelle has also been used to prepare nanosize rod-shaped copper .

Nanoparticles can be obtained from micellar solutions of anionic surfactants using as counter ion,the ion of the metal that is to be formed as nanoparticles. The most commonly used surfactant for the purpose is dodecyl sulfate and a wide variety of metal salts have been used as counter ion. Copper nanoparticles have been synthesized from a micellar solution of copper dodecyl sulfate using sodium borohydride as reducing agent. it has been found that the particle size can be varied by using a mixture of copper dodecyl sulfate and sodium dodecyl sulfate as surfactant. Increasing the amount of

sodium dodecyl sulfate while keeping the concentration of copper dodecyl sulfate constant, gave smaller particles, most likely as a result of fewer Cu (II) ions per micelle.

Metal nanoparticles can also be synthesized in a water-hydrocarbon two-phase system using a phase transfer agent to transport the metal ion into the organic phase, a method developed for gold and silver particles. The phase transfer agent is usually a lipophilic cationic species, such as a tetraalkylammonium salt, which gives an ion pair that is readily soluble in the organic phase. The phase transfer agent also transfers water into the nonpolar phase and small metal particles are generated in these aqueous droplets. A stabilizing agent is needed in order to control the growth of the nanoparticles.

Mesoporous materials are defined as materials that have at least one dimension in the size range 2-50 nm. Synthesis of Mesoporous materials by the use of surfactants as structure-directing agents started around 1990 when it was demonstrated that mesoporous silica could be obtained by the templating action of cationic surfactants (Stephen et al., 2009). A tetraalkylorthosilicate, such as tetraethylorthosilicate (TEOS),was used as silica precursor and silica with pores in the mesoporous regime and with relatively narrow size distribution could be obtained by proper choice of surfactant, surfactant concentration, and pH. Either basic or acidic conditions can be used for hydrolysis of the precursor molecule, which initiates the polymerization. Surfactant mainly been used for the preparation of mesostructured hexagonal materials but materials with a bicontinuous cubic structure have also been synthesized starting from surfactant liquid crystals

with cubic geometry. Nonionic surfactant, in particular block copolymers made up of hydrophilic polyoxyethylene segments and hydrophilic polyoxypropylene segments (Figure 7).

A somewhat different approach for the formation of Mesoporous materials so-called evaporation-induced surfactant self-assembling (EISA) technique developed by Brinker and colleagues. Here a mixture of surfactant, acid, and a metal alkoxide precursor, which have the compositions corresponding to the wanted liquid crystalline phase, is prepared.The mixture is dissolved in excess of ethanol, which results in a low viscous solution. Then, upon evaporation of ethanol, the liquid crystalline phase is reformed. For example, partly crystalline Mesoporous titania thin films, with silver nanoparticles incorporated within the pores, supported onto glass slides have been produced (Andersson et al., 2005) Figure(8).

Kai Man K. Yu, etal (2003) synthesized Pd nanoparticles with controllable sizes within a silica matrix using solid-supported surfactants in supercritical CO_2. XRD, HRTEM and CO chemisorption data show that unformly sized Pd nanoparticles are evenly distributed within the porous silica and are chemically tethered by surfactant molecules [poly(oxyethylene stearyl ether) and fluorinated poly(oxyethylene)]. It is postulated that tiny solid-supported surfactant assemblies act as nano-reactors for the template synthesis of nanoparticles.

A sol–gel method assisted with triblock copolymer surfactant P123 was reported to synthesize uniform distributed nano-sized $LiCoO_2$. Comparing the results of XRD measurement with that observed by SEM it was found that $LiCoO_2$ particle is

Figure.8 TEM micrographs of mesoporous titania with incorporated silver. The left picture shows a bright field (BF) micrographs of the highly ordered mesoporous cubic structure of titania. The dark spots are silver particles situated within the titania. The right picture shows a dark field (DF) micrographs taken on mesoporous cubic titania. Here the bright spots ara titania crystallites and the very dark spots are silver.
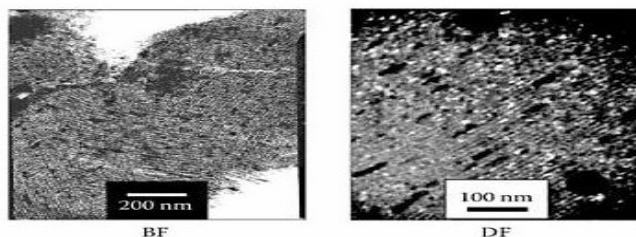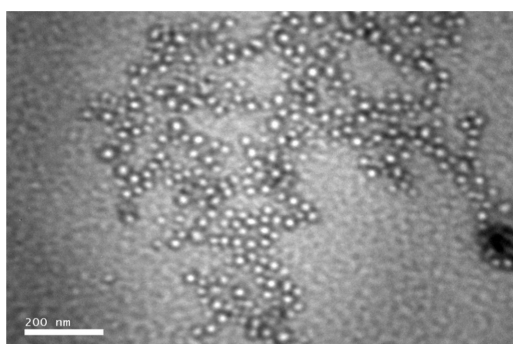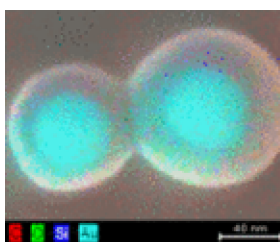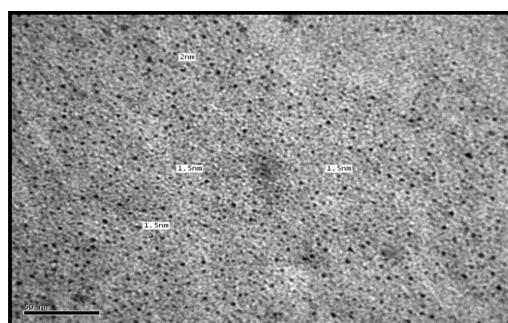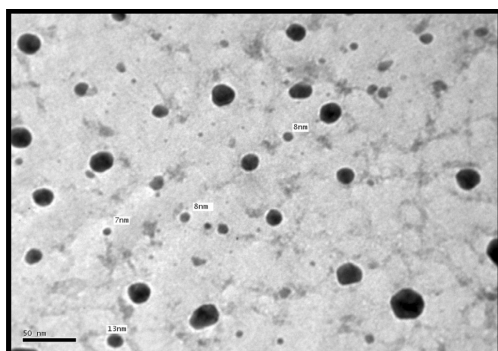
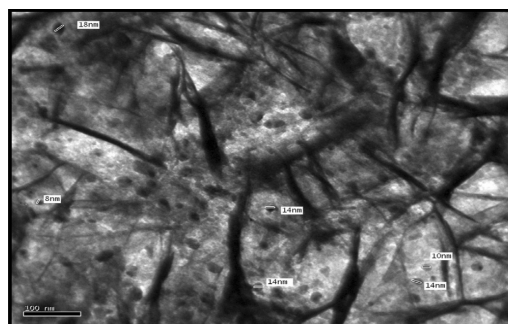

Figure 9: Gold-containing nano-particle

TEM of the gold nano particles

TEM of mercaptopropane sodium sulfonate (C3).

TEM of mercaptooctane sodium sulfonate (C8)

TEM of mercaptodecane sodium sulfonate (C10)

Figure.10 High energy ball milling.

formed from a single crystal, which can be attributed to the effect of soft template P123. The size of nano-LiCoO$_2$ particles increases with the increase of synthesizing temperature. Nano-LiCoO2 prepared at 750 °C exhibits high electrochemical performance with an initial discharge capacity of 149 mAh g−1, and good cycling stability. It was found that the novel properties of nano-LiCoO$_2$ particles provide the potential to prepare ultra-thin-film electrodes using computer jet-printing method, and might be used in thin-film lithium-ion batteries.

On the other hand, Preparation of ZnO nanoparticles by a surfactant-assisted complex sol–gel method using zinc nitrate. ZnO nanoparticles with a pure wurtzite structure were obtained after calcination at 773 K. The effect of the citric acid concentration, the pH, and the surfactants on the average particle size and morphology of the ZnO nanoparticles were investigated using X-ray diffraction and scanning electron microscopy. ZnO nanoparticles with a uniform size distribution were obtained using polyethylene glycol (PEG) 2000 as a surfactant. During sintering, the ZnO nanoparticles revealed isotropic growth below 1,373 K and anisotropic growth above 1,473 K. The particles, activation energy was calculated to be 140 kJ/mol between 773 and 1,373 K.25

Monodispersed silica-coated rhodium nanoparticles were synthesized by using the w/o microemulsion of polyoxyethylene cetyl ether / cyclohexane / water system. By hydrolysis of tetraethyl orthosilicate in the presence of rhodium complex nanoparticles followed by thermal treatment, the silica-coated metallic rhodium nanoparticles were obtained in the microemulsion. In the composite nanoparticles, a metallic rhodium particle with a diameter of 4 nm was located nearly at the center of a spherical silica particle. The thickness of silica layer was 14 nm.

Huiping Shao; etal. (2005) were prepared iron pentacaronyl by thermal decomposition under 180°C with 0.256M and 0.085M oleylamine as a surfactant. Sizes of the synthesized iron nanoparticles are from 4.8nm to 10.9nm depending on the decomposition times in the range from 10 to 60 min. The surfactant concentration is a key factor for controlling the size and shape of iron nanoparticles.

The synthesized iron particles without surfactant are flocculated to be clusters of 20-50 nm. In the case of using 0.0425M surfactant, the obtained particles are almost sphere. While oleylamine concentration was added up to 0.085M, several iron nuclei are agglomerated together regularly. It is confirmed that the synthesized iron particles are amorphous, but the surface of the particles is easily oxidized and to be spinel structured iron oxide by HRTEM.

On the other hand , Lai JI,etal.(2005) controlled the size of magnetic nanoparticles by adjusting the surfactant/solvent ratio. Gamma-Fe_2O_3 nanoparticles of 5.6 and 12.7, and Fe(0) nanoparticles of 22.3 nm in diameter were prepared, all having spherical shape and uniform size as confirmed by TEM. Mossbauer spectra confirmed Fe^{3+} for the 5.6 and 12.7 nm particles and Fe(3+) and Fe(0) for 22.3 nm particles, in good agreement with synchrotron XRD patterns.

Xu XJ, etal. (2003) have been successfully synthesized nanosized polystyrene (PS) latexes stabilized by the mixture of cationic/cationic, anionic/anionic, or anionic/cationic surfactants of various types with high weight ratios of PS to surfactant (ca. 10:1) by a semicontinuous microemulsion polymerization process. For cationic or anionic systems, spherical latex particles with a weight-averaged diameter (Dw) ranging from about 22 to 53 nm were nearly linearly dependent on the weight ratio of the mixed surfactants with similar charges. Their particle size distributions were rather uniform (Dw/Dn < 1.20). For a system with oppositely charged surfactants at nonequimolar ratios, it could produce stable PS particles up to 94 nm in diameter. High molar masses (Mw) of PS ranging from 1.1 to 1.9 x 10(6) g/mol could easily be obtained for all three systems investigated. For both cationic/cationic and anionic/anionic surfactant systems, the number of PS particles per milliliter of latex (Np) generated in the very early stage of O/W' microemulsion remained rather constant throughout the polymerization. This was controlled by using only 1 wt% of mixed surfactants and the continuous addition of a small amount of styrene. The present polymerization method allows one to synthesize nanoparticles of PS or other polymers of high polymer/surfactant weight ratios at some particle sizes that are unable to achieve them with a single type of surfactant.

While Woo J. K., etal. (2008) were prepared polypyrrole nanoparticles by emulsion polymerization, and the surface charge of PPy nanoparticles was controlled by the mixed surfactant system of dodecylbenzene sulfonic acid and isooctylphenyl ether. The shape and size of nanoparticles prepared could be controlled by changing concentration of surfactant. In addition, it was confirmed that the nanoparticles with good conductivity could be obtained by this preparation method. Consequently, well dispersed PPy nanoparticles with 60-100 nm in diameter with cubic shape were obtained.

The barium compound nanoparticles were synthesized using the microemulsion formed by AOT as an anionic surfactant and iso-octane as an organic solvent. Chromate, sulfate, or carbonate-containing microemulsion solution and Ba(AOT)2 reverse micelle solution were mixed. After a few days, the morphology of the product material was observed using TEM. Then, bundle of the nanowire, chain structure of

the nanorod, superlattice structure of the nanodot, and dispersed nanodot were synthesized by changing material concentration and material molar ratio. It has been shown that the aspect ratio of the generated particles decreased with increase in the anionic ion concentration. In contrast, the aspect ratio did not change even if the barium ion concentration changed. The surfactant AOT has selectively adsorbed on the specific crystal faces and suppressed their crystal growth. And, the generated particles were self-organized by the hydrophobic interaction of hydrophobic group of the AOT molecule adsorbed onto the particle. In conclusion, it was clarified that the supersaturation ratio and the particle–surfactant interaction were important factors for controlling the shape and size of the inorganic Nanoparticles.

NiO nanoparticles synthesised by chemical precipitation and effect of applied surfactant on distribution of particle size. and the following surfactants (for reduction in particle size). Applied surfactants are in two kinds: polymeric (PVP, PEG) and cationic (CTAB) surfactants, 1.0 gram.

CdSe and CdSe/CdS core/shell nanoparticles (NPs) were synthesized by using Gemini surfactant, 1,10-bis(alpha-hexadecyl pyridine) decamethylene dibromide (abbreviated Py-16-10-16), as a soft template. Subsequent analysis revealed that the as-synthesized CdSe NPs and CdSe/CdS core/shell NPs were highly luminescent with quantum yields of 18% and 35%, respectively, compared with Rhodamine 6G (95%). Furthermore, when the nanoparticles were conjugated with bovine serum albumin (BSA) in PBS buffer solution (pH 7.40), the fluorescence intensity of the BSA system was quenched by the addition of CdSe/TGA or CdSe/CdS/TGA NPs, while the fluorescence intensities of CdSe/TGA and CdSe/CdS/TGA NPs were enhanced by the addition of BSA. This enhancement and quenching of the fluorescence intensity by conjugating with BSA could be used to determine the albumin concentration (Chang et al., 2009).

Sb_2O_3 nanoparticles, nanowires, and nanoribbons have been selectively synthesized in a controlled manner under mild conditions by using CTAB as a soft template. By adopting $Sb(OH)_4-$ as an inorganic precursor and the concentration of CTAB as an adjusting parameter, morphologies of Sb_2O_3 nanostructures can be selectively controlled. Typically, CTAB < 0.15 mmol favors the formation of nanoparticles (product one or short form P1); when the concentration of CATB is in the range 0.15-2.0 mmol, nanowires (P2) dominate the products; nanoribbons (P3) form above the concentration of 2.0 mmol, and when the concentration of CTAB goes further higher, treelike bundles of nanoribbons could be achieved. The method in the present study has potential advantages of easy handling, relatively low-cost, and large-scale production. The facile and large-scale synthesis of varied Sb2O3 nanostructures is believed to be useful for the application of catalysis and flame retardance.

Synthesis and self-assembly of gold nanoparticles using gemini surfactant as a phase transfer reagent and a stabilizer by Jian Xu; etal. (2006). They consist of a core of gold (Au) with a shell of mainly silicon (Si) and oxygen (O) – glass.

Nonspherical gold nanoparticles were prepared in water by the reduction of $AuCl_4$ in the presence of multichain

cationic surfactants, which consisted of some hydrophobic and some hydrophilic groups. It is known that those surfactants have exhibited good physicochemical properties as lower critical micelle concentrations. The monomeric or polymeric surfactants served as a stabilizer of the synthesized nanoparticles, and the nanoparticles have dispersed in water for several months. Electronic absorption spectra of the dispersed solutions showed the different plasmon peaks associated with spherical and/or nonspherical gold nanoparticles. The spherical-, rod- and polygonal- shaped nanoparticles were characterized by transmission electron microscopy (TEM). Shape and yield of nanoparticles by using monomeric or polymeric surfactant was discussed.

On the other hand, gold nanoparticles were prepared in water by $NaBH_4$ reduction of $AuCl_4$ in the presence of quaternary ammonium salt-type trimeric surfactants, which consisted of three hydrophobic and three hydrophilic groups. It is known that those surfactants have exhibited good physicochemical properties as lower critical micelle concentrations (cmc). The surfactants served as a stabilizer of the nanoparticles, which had dispersed in water for several months. Hydrocarbon chain length of the surfactant had an influence on the diameter of Nanoparticles.

Applications of surfactant in nanotechnolgy

Applications of Nanoemulsions

Nanoemulsions in agrochemicals

Nanoemulsions have a variety of applications in agrochemical Industry.To minimize the side effects of excessive use of agrochemicals on the ecosystem, chemicals with greater specificity and less persistence are developed. The ease of handling and lower requirement of smelly solvents go in favour of the use of nanoemulsions. However, increased efficacy of insecticides when applied as 'nanocolloidal aqueous emulsion' instead of microemulsions has also been demonstrated. O/W nanoemulsions of organic, water insoluble phenoxy herbicides optionally dissolved in a hydrocarbon solvent have been shown to be appreciably more effective than the corresponding emulsions in the control of plant growth. the formulation of agrochemicals using surfactants is advantageous. The much finer droplet size of the nanoemulsion leads to higher penetrability, much larger contact area of the active substance to the treated surface and a much more even distribution during application. The infinite stability of the nanoemulsion and the high concentration of surfactants generally needed for a formulation are advantageous. A definite relationship exists between herbicides and surfactant structures for mixed herbicide penetration.

Nanoemulsions as lubricants, cutting oils and corrosion inhibitors

Nanoemulsions or reverse micellar solutions are in use as lubricants, cutting oils and corrosion inhibitors for several decades. The presence of surfactant in nanoemulsion causes corrosion inhibition .The coating application area is a very promising and rapidly-growing field of microemulsion technology, because the nanoemulsified resins overcome many the shortcomings of the more traditional water-based systems without creating the health and pollution problems and flammability hazards of the solvent-based

coatings. Due to their stability and small droplet size, nanoemulsions are ideal, where stability and homogeneity of the finished product is desired. Paint formulations using nanoemulsions have shown higher scrub resistance, better colour intensity and more stain resistance than those prepared by emulsions. In principle,three different possibilities of using nanoemulsions exist for coating applications: (1) for producing nanodispersions by using nanoemulsified monomers, (2) for transferring non-water-soluble polymers into water, and (3) for obtaining specific effects by polymerization in w/o system.

Nanoemulsion and solution approaches to nanoparticle iron production for degradation of trichloroethylene

In this study, nanoscale iron particles were synthesized using the microemulsion method and the properties were compared with the particles produced by the solution method. The nanoparticles were characterized by using the transmission electron microscope (TEM) and powder X-ray diffraction (XRD). The water-in-oil (w/o) microemulsion system was made up of n-octane, cetyltrimethyl-ammonium bromide (CTAB), butanol and water, and was characterized by measuring the conductivity of the solution and interfacial tension between the surfactant solution and the n-octane. Interfacial tension between the n-octane and the CTAB aqueous solution was reduced to less than 6 dyn /cm with the addition of butanol, a co-surfactant used in this study. The average diameter of synthesized iron nanoparticles using the microemulsion method was less than 10 nm, which was much smaller than the particles produced by the solution method. The performance of the nanoiron produced in the laboratory

was studied by dechlorinating trichloroethylene (TCE), a dense non-aqueous phase liquid (DNAPL) and listed as a priority pollutant by the US EPA. The degradation rate of TCE by the nano iron particles produced in the laboratory was quantified and compared with a commercially available nano iron product (Li et al., 2003).

Application of Nanoemulsions in Pharmaceutics

The advantages of nanoemulsion as a novel vehicle of the drug delivery system, the roles of the ingredients and the application of various methods of administration in pharmaceutics were systematically reviewed. The application of nanoemulsions in drug delivery systems including transdermal, mucosal, oral and injection delivery systems was better than ordinary emulsions. Nanoemulsions, with a very good prospect in pharmaceutics in the future, had many good characters such as good solubilization to indissolvable drugs, delayed release, targets and high bioavailability.

Antimicrobial Nanoemulsions

An unique aspect of the nanoemulsions is their selective toxicity to microbes at concentrations that are non-irritating to skin or mucous membrane. This safety has been tested in several animal species and verified during human clinical trials. The safety margin of the nanoemulsion is due to the low level of detergent in each droplet, yet when acting in concert, these droplets have sufficient energy and surfactant to destabilize the targeted microbes without damaging healthy cells.

Prevention of murine influenza A virus pneumonitis by surfactant nano-emulsions

Non-ionic surfactant nano-emulsions have extensive anti- microbial activity and biocompatible with skin and mucous membranes at effective concentrations. Two nano-emulsion formulations (8N8 and 20N10) made from soybean oil, tributyl phosphate and Triton X-100, were tested for their ability to prevent murine influenza virus pneumonia in vivo.

Role of surfactants in controlling particle size of polymeric nanocapsules containing penicillin-G in double emulsion

Preparation, characterization and drug release behavior of loaded polybutyl adipate (PBA) nanocapsules with penicillin-G are described here. The nanocapsules were produced using a double emulsion solvent evaporation technique, using dichloromethane as an organic solvent and Tween , Span as surfactants . Penicillin-G loaded nanocapsules with low concentrations of both surfactants tend to have higher burst release. Under optimum formulation conditions, the encapsulation of penicillin-G can reach up to 60% and the burst release can also fall below 45%. In this case, the fact that the nanocapsules have only 130 nm diameter will be important (Sepideh Khoee and Morteza Yaghoobia, 2010).

Self-Assembling Thiol Surfactants on Gold Nanoparticles

Gold nanoparticles have been drawing a lot of attention because of their novel physicochemical properties, especially their special nonlinear optical properties and surface-enhanced Raman scattering effect, and potential applications in biology, catalysis, photocatalysis, and microelectronics. High affinity of organic functional groups like—SH, _CN, _COOH, _NH2 for metallic surfaces such as Au, Cu, Ag, Pd, Pt, Hg have motivated several research groups to focus on using this phenomena for industrial applications. Self–assembled monolayers of organosulfur compounds like thiols, sulfides and disulfides on the surface of coinage metals like Cu, Ag and Au, have attracted much attention. The thiol molecules absorb readily from solution onto the gold substrate, creating a dense monolayer with the head group pointing outwards from the surface. By using thiol molecules with different head groups, the resulting chemical surface functionality can be varied within a wide range. In addition, it is also possible to chemically functionalize the head groups by performing reactions after assembly of the SAMs. More recently, inorganic synthesis has been investigated using gold nanoparticles with ionic liquids such as thiol anionic surfactants (i.e., mercaptoethanesulfonic acid, sodium salt). The ionic liquids have increasingly been drawing attention in research mainly due to their ''green solvent'' properties. These compounds exist as solventless cations and anions at room temperature. Ionic liquids have a variety of applications due to their tunable properties including polarizability, hydrophobicity, and solvent miscibility which are affected by cation and anion present in the compound. The adsorption of surfactant-like molecules to nucleated nano-crystals lowers the free energy of the surface and, therefore, the reactivity of the particles. The ratio of surfactant to metal precursor can control the size distribution of the nanoparticles. The mechanism by which this ratio controls the nucleation

events and limits the growth of the particles is understood in general qualitative terms. The steric bulk of the surfactants provides a physical barrier that prevents the metal surfaces from contacting each other directly. They can also change the surface charge of a cluster and thus change its stability toward aggregation (Azzam et al., 2009).

Role of surfactants in carbon nanotube toxicity:

Synthesized carbon nanotubes, especially single-walled carbon nanotubes (SWCNTs), are in the form of bundles with other impurities such as catalyst particles and amorphous carbon debris. In order to be useful for many types of applications, for instance in nanoelectronic devices or biomedical applications, SWCNTs need to be purified and dispersed into individual nanotubes. One method to do this is by surfactant stabilization of the hydrophobic nanotube surface, which overcomes the van der Waals forces among the nanotubes and results in suspensions of individual SWCNTs. (Guobin et al., 2009). Several commercial surfactants, such as sodium dodecyl sulfate (SDS), sodium cholate (SC) and sodium dodecylbenzene sulfonate (SDBS) have been demonstrated to efficiently disperse bundled single-walled carbon nanotubes into aqueous suspensions of individual nanotubes. However, there has been no systematic study on the toxicity of nanotube conjugates with the extensively-used SDS, SDBS, and SC surfactants. It is critical to understand the cytotoxicity of the nanotube-surfactant conjugates since these reagents are increasingly being used in industry and laboratories. The toxicity of a surfactant may not only cause health issues for those working with carbon

nanotubes, but may prove toxic to cells when used as non-viral transporters for biomolecules including DNA, siRNA and proteins for therapeutic purposes.

The nanotubes were purified without metallic catalyst particles and amorphous carbons. Both catalyst particles and amorphous carbon have been demonstrated to influence cell viability. The experiments show that the toxicity of nanotube conjugates appears to be controlled by the specific molecules attached on the nanotube surfaces. This means, one criteria whether nanotubes are toxic or not depends on how the nanotubes are purified and dispersed as well as the surface cargos that they may carry. Our experiments also demonstrate that, in contrast to SDS and SDBS, SC is an environmental-friendly reagent to be used for dispersion and purification of nanotubes.

In the preparation and processing of nanocomposites, where carbon nanotubes (CNTs) are introduced into polymeric matrices as a reinforcing filler, microscale aggregation of the CNTs is a major issue.

Researchers at The Hebrew University of Jerusalem and the Weizmann Institute of Science in Israel have analyzed the effect of surfactants, as well as surface oxidation and functionalization, on the dispersion of surface-modified multiwalled CNTs in polymers .

Due to the vast number of combinations of polymers and mixing conditions, it would be beneficial to have a handy set of guidelines to help select the optimum mixing variables," says Gad Marom of The Hebrew University. The researchers suggest general guidelines to produce

uniform CNT dispersions using a dispersive agent and/or surface treatment in both water-soluble and water-insoluble polymers.The team found that the behavior of a surfactant in dispersing the CNTs is similar to that in the case of solid particles, i.e. classical colloidal chemistry.Since surfactant effects depend strongly on the medium's chemistry, aqueous and organic polymeric systems of CNTs should, in principle, obey different colloidal processes. However, a common factor is that surfactants having long tail groups and more unsaturated carbon-carbon bonds greatly contribute to stabilizing the CNT dispersions and reducing the size of CNT agglomerates.In a water-soluble polymer, e.g. poly(ethylene glycol), cationic surfactants show some advantage, owing to their preferential attraction to negatively charged CNT surfaces. In a water-insoluble polymer, e.g. polypropylene, a high-quality CNT dispersion is promoted by a nonionic surfactant containing a branched tail.To understand the surface-charge effects, zeta-potential measurements were made. CNT dispersion was quantified by particle-size analysis, and the nucleating ability of the surface-modified CNTs was estimated by calculating the crystallization temperature and the degree of crystallinity from differential scanning thermograms.

Dispersion of carbon nanotubes (CNTs) is a challenging task for their utilization in nanoscale device applications. This account reports a comparative analysis on dispersion of multiwalled carbon nanotubes (MWNTs) with four surfactants-Triton X-100, Tween 20, Tween 80, and sodium dodecyl sulfate (SDS). Among the four surfactants, Triton X-100 and SDS provide maximum and minimum dispersion, respectively.

Dispersion of MWNTs has been characterized with UV-vis spectroscopy and transmission electron microscopy (TEM). TEM results are in agreement with the UV-vis measurements. The experimentally observed trend of dispersing power of surfactants is consistent with their chemical structures. An optimum CNT-to-surfactant ratio has been determined for each surfactant. This parameter is shown to affect the nanotube dispersion significantly. Surfactant concentration above or below this ratio is shown to deteriorate the quality of nanotube dispersion. TEM analysis of a high-surfactant-concentration sample enables us to construct a plausible mechanism for decrease in CNT dispersion at high surfactant concentration, consistent with the UV-vis observations. Temperature stability of the surfactant is another important factor affecting the quality of CNT dispersion (Rastogi et al., 2008).

Role of micelle in decreasing the side effect for anticancer drug

Using micelle or microsphere as a carrier of anticancer drug is to reduce side effects of cancer treatment by inserting anticancer drug into micelle or microsphere and letting it release slowly. When anticancer drug is administrated separately, it works in a short period in large quantities , by which side effects are caused. Micelle is a good try to reduce those side effects by inducing slow release of the anticancer drug.

Nanoparticles, drug carriers in the sub-micron size range, can enhance the therapeutic efficacy of encapsulated drug by increasing and sustaining the delivery of the drug inside the cell. However, the use of nanoparticles for small molecular

weight, water-soluble drugs has been limited by poor drug encapsulation efficiency and rapid release of the encapsulated drug. Here we report enhanced cellular delivery of water-soluble molecules using novel Aerosol (AOT)-alginate nanoparticles (Chavanpatil et al., 2007).

Poor drug encapsulation efficiency and rapid release of the encapsulated drug limit the use of nanoparticles in biomedical applications involving water-soluble drugs. We have developed a novel polymer-surfactant nanoparticle formulation, using the anionic surfactant Aerosol (AOT) and polysaccharide polymer alginate, for sustained release of water-soluble drugs. Particle size of nanoparticles, as determined by atomic force microscopy and transmission electron microscopy, was in the range of 40-70 nm. Weakly basic molecules like methylene blue, doxorubicin, rhodamine, verapamil, and clonidine could be encapsulated efficiently in AOT-alginate nanoparticles. In vitro release studies with basic drug molecules indicate that nanoparticles released 60-70% of the encapsulated drug over 4 weeks, with near zero-order release during the first 15 days. Studies with anionic drug molecules demonstrate poorer drug encapsulation efficiency and more rapid drug release than those observed with basic drugs. Further studies investigating the effect of sodium concentration in the release medium and the charge of the drug suggest that calcium-sodium exchange between nanoparticle matrix and release medium and electrostatic interaction between drug and nanoparticle matrix are important determinants of drug release. In conclusion, we have formulated a novel surfactant-polymer drug delivery carrier demonstrating sustained release of water-soluble drugs.

Anticancer efficacies of nanoparticles loaded drugs

Cisplatin

in is a potent anticancer drug with low solubility in water . A new type of highly stable polymer micelles , namely core-surface-cross linked nanoparticles (ScNPs) made from ampliphilis brush copolymers were evaluated as the carrier of cisplatin . Cisplatin could be loaded in the ScNPs with poly (varepsilon-caprolacton) (pcl) cores and hydrophilic polyethyleneglycol (PEG) shells with high loading efficiency (approximately 90%). Measurements indicated that cisplatin encapsulated in the SCNPs had much enhanced cytotoxicity to the cancer cells compared to free cisplatin (Xu et al., 2006).

Paclitaxel (Taxol)

Paclitaxel (Taxol) is one of the best antineoplastis drugs found from nature in the post decades . Like many other anticancer drugs , There are difficulties in its clinical administration due to its poor solubility.However , nanoparticles of biodegradable polymers can provide an ideal solution to the adjuvant problem and realise a controlled and targeted delivery of the drug with better efficacy and fewer side – effect (Mu L. and Feng, 2003).

Doxorubicin

Development of a new drug carrier made from alginate . Evalution of the drug – loading capacity was done with doxorubicin as a drug model . The result indicate that alginate nanoparticles are interesting carriers because the drug – loading capacity could be > 50 mg of doxorubicin per 100 mg of alginate (Rajaonarivony et al., 1993).

Nanotechnology in Soft Materials: Application for Cosmetics, Foods, Personal Care, Pharmaceutical and Oil Industries

Nanotechnology applications into Soft Materials containing colloids, surfactants, proteins and block copolymers have an extremely large range of industrial uses. Soft materials contain nanometer to micron size structures, which can be designed in an increasingly wide range of shapes. Their properties are determined by these soft nanostructures, and can be remarkably different to the properties of the unstructured materials. One big advantage of these soft materials is that under suitable conditions the molecules they contain will self-assembly to form nanoscale structure, often with little or no energy input. This tutorial will provide an introduction to nanotechnology in soft materials (also known as colloid science, mesoscale phenomena, soft matter physics, complex fluids, or polymer science!). We will highlight current and potential applications in cosmetics, foods, paint, soaps and detergents, pharmaceutical delivery, the oil industry; and also the use of self-assembled soft nanostructured materials to create hard nanoparticles, or to create hard nanoscale structures on surfaces (Bidyut K. P.and Satya, 2001).

On the other hand, many soft or fluid consumer products, such as foods, paints, detergents, personal care products, and cosmetics contain nanometer to micron scale structures. These structures are formed by the spontaneous or directed self-assembly of surfactants and polymers. In many cases complex mixtures are required to create the desired structures and performance. These materials are difficult to formulate, and challenging to characterize; but scientists in these industries, and in the academic groups focusing on these areas, have developed considerable expertise in this area. New insights and techniques have the potential to revolutionize product design. This knowledge is being applied in new areas such as drug encapsulation, solubilization and delivery, in oil recovery, environmental remediation, and in new "active" cosmetics, nutraceuticals, antimicrobials and smart materials.

Present work

Enhancement of the Antitumour Activity for the Synthesised Dodecylcysteine Surfactant using Gold Nanoparticles

The surfactant dodecylcysteine hydrochloride was synthesised. The antitumour activity of the prepared surfactant without and with the gold nanoparticles was investigated. The results show that the antitumour activity of the prepared surfactant was enhanced with the presences of the gold nanoparticles.

Copper (II)-surfactant complex and its nano analogue as potential antitumor agents

The in vitro anticancer activity of copper cetyl trimethyl ammonium bromide (Cu-CTAB)-loaded cyclodextrin nanoparticles on Ehrlich ascites carcinoma (EAC), colon cancer cells (HCT 116), liver cancer cells (HepG-2), breast cancer cells (MCF-7) and cervix cancer cells (Hela) was investigated using MTT due assay. The nano analogue was synthesized by physical loading using grinding with ball mill. The anticancer activity between MCF-7, Hela, Hct-116 of Cu (II)-CTAB and Cu (II)-CTAB-loaded cyclodextrin

nanoparticles are nearly the same and that indicates the anticancer activity of the loaded Cu (II)-CTAB nano compound is higher four folds than the free Cu (II)-CTAB.

Electrochemical behaviour of carbon steel in acid chloride solution in the presence of dodecyl cysteine hydrochloride self-assembled on gold Nanoparticles

The maximum inhibition efficiency approached 76.6% in the presence of 175 ppm of dodecyl cysteine and 90.8% in the presence of the same concentration of dodecyl cysteine hydrochloride self-assembled on gold nanoparticles.

Characterization of Cobalt Oxide Nanocatalysts Prepared by Microemulsion with different Surfactants, Reduction by Hydrazine and Mechanochemical Method

Cobalt oxide(Co_3O_4) nanoparticles were prepared by different techniques and the results revealed that all samples obtained from different methods were nanosized particles.

Preparation of Ni- and Cu-Oxide Nanocatalysts by Microemulsion Method using Surfactant and Their Characterization

The decomposition of hydrogen peroxide over Ni- and Cu-Oxide Nanocatalysts showed that they have obviously higher catalytic activities as compared with nickel oxide and copper oxide prepared by the conventional precipitation method.

Alkaline Hydrolysis of TNT in Micellar System (Sanaa M.Soliman , 2010)

Alkaline hydrolysis of TNT using mixture of nonionic surfactant micelles and anionic

surfactant showed higher degradation than that with a cationic surfactant.

Future work

Application of surfactant nanoparticles as stationary phases in gas chromatography

Characterizes
Surfactants and polymeric surfactant nanoparticles are promising to be good adsorbants and can be used as stationary phases in GC packed and capillary columns. May be due to their specific characteristics and it can gives good resolution for solving some petroleum problems such as separation of isomers (xylenes,cresol and other compound which have the same boiling point and same molecular weight), and separation of macromolecules (compounds of high molecular weight).

Nanocomposite thin film coatings. Characterizes

Corrosion usually takes place and degrades material surfaces based on environmental chemistry.
These include surface treatment methods, nanocomposite thin film coatings, the corrosion performance of materials is significantly improved as compared to materials processed using conventional methods.

Nanotechnology The Next Revolution For Wastewater Treatment (TNT Contaminants)

At present there are clear opportunities for nanoscience and nanotechnology in industry. Some applications can be anticipated and can result in targeted advances in technology. However, new scientific advances usually lead to new

technological innovations that might not have been predicted at the outset. At present the industry is at a crossroads. It can pass by and hope to exploit developments in nanotechnology as they emerge serendipitously or otherwise in the future, or it can embrace these new skills and set targets to drive scientific advances in pursuit of specific goals.

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