Summary

"Nanotechnology" covers many aspects of research in which the characteristic dimensions of the materials of interest are less than about a micron, or 1,000 nanometers (nm). In this size range, unique physical, optical and electronic properties are said to be exhibited that are not present in the bulk phase. This phenomenon opens up a completely new perspective for materials design that benefits from the introduction of not only particle size but also particle morphology as new powerful parameters. The physical and chemical properties of metal nanoparticles depend upon several factors such as the particle size and dispersity, the surface of the particles, the shape of the particles and their organization. A brief description of the present work highlights our significant contribution in this potential area of research.

A brief literature survey presented in the beginning fairly describes the importance of metal nanoparticles, their preparation, characterization and the size dependent physical and chemical properties and shows the opportunities in this area for innovative research and development. In the scope of this work we have considered synthesis, structure, stability and morphology of Ru, Pt, Ag and Au metal nanoparticles. We have used γ-radiolysis, UV photolysis, pulse radiolysis and chemical reduction methods for the preparation using i) polymers, ii) solid supports like zeolites, iii) surfactants or co-ordination ligands and iv) solvents or anions as stabilizers. The work has been described in different chapters.

The basic principles in synthesis and characterization techniques have been explained. The radiolysis, photolysis and chemical reduction methods have been described. The systems have been carefully chosen to include i) polymers, ii) solid supports like zeolites, iii) surfactants or co-ordination ligands and iv) solvents or anions and also their modified forms as stabilizers. Different chapters have been organized based on the nature of these stabilizers. The nanomaterials were characterized by UV-vis, XRD, TEM, SEM, XPS, TPR, and FTIR spectroscopy techniques.

Ru and Pt metal nanoparticles are used as catalysts for various industrially important reactions such as hydrogenation, hydrogenolysis, isomerization and in fuel cells. They are needed in precise size and shape devoid of impurities for better performance. In the present work Ru, Pt and bimetallic Ru-Pt nanoparticles of various
metal compositions have been prepared by $\gamma$-irradiation in aqueous solution. Polyvinylpyrrolidone (PVP) has been used as capping agent for the stabilization of particles. The results show a clear indication of the formation of Ru, Pt and Ru-Pt alloy particles. Oxide phases were not detected in the bulk, however surface oxide formation was observed. The particles of different sizes were obtained based on different parameters. We have concluded that the bimetallic Ru-Pt nanoparticles consist of alloyed particles as well as monometallic Ru and Pt nanoparticles.

Ru and Pt metal nanoparticles stabilized on solid supports like zeolites are potentially useful catalysts. They are conventionally prepared by impregnation and ion exchange followed by chemical or hydrogen reduction. During these severe conditions of reduction, nanometal species migrate from cationic site-to-site and also to the surface. Therefore changes that take place during the evolution of Pt, Ru and Pt-Ru alloy nanoparticles, the acidity of the zeolite and their mutual influence cannot be understood precisely. In order to better understand this complex system we have used $\gamma$-irradiation method, which is very facile and devoid of such undesirable influences. The catalytic activity in hydrogenation of benzonitrile was tested considering its industrial importance. The influence of Ru on the physico-chemical properties particularly on acidity and catalytic activity of Pt/NaY zeolite catalysts are presented. Similar studies have not been reported so far. As prepared, the samples consisted of Ru$^0$, Pt$^0$ and (Ru-Pt)$^0$ bimetallic alloy species associated with Bronsted acidity sites which are chemically anchored as $\text{H}^+$ - metal adducts both in sodalite and supercages of zeolite. The $\text{H}^+$-metal adducts break down on heating the sample resulting in the reduced acidity and migration of Ru and Pt crystallites in to supercages and on the surface partly forming oxide species. The liquid phase catalytic hydrogenation of benzonitrile over Ru/NaY gives selectively benzylidene benzylamine and dibenzylamine over Pt/NaY zeolite. Similar patterns in conversion and selectivity have never been reported in hydrogenation of nitriles over any zeolite-based catalysts.

Surface modification of metal particles using functionalized capping molecules has led to the exciting possibilities for anchoring colloidal particles to metal surfaces. Attempts have been made to stabilize metal and semiconductor nanoparticles in the presence of biologically important compounds such as DNA, proteins, and biotin (vitamin H). It has been reported that biotin has three potential binding sites for metal...
ions i.e. the carboxylate, the thioether and the ureido group. The colloidal silver particles capped with biotin have been studied for their aggregation behavior in the presence of avidin. As Ag metal has potential bactericidal properties, it is important to study the formation and growth of Ag metal nanoparticles and its interaction with biologically important compounds such as biotin in aqueous and non-aqueous solvents. Pulse radiolysis is an excellent tool for the investigation of abnormal valence states of metal ions and small clusters in aqueous solutions. In the present study we report for the first time the formation of Ag nanoparticles in the presence of biotin, and their self-assembly into long fiber-like structures. As the formation of any shape/structure might depend on the initial clusters, the growth mechanism of the initial Ag clusters was elucidated by pulse radiolysis technique. Ag nanoparticles in the presence of biotin molecules formed long fiber-like structures of 4 µm long with a thickness of 1 µm. These Ag nanoparticles were found to be highly crystalline in nature. The cross-linking of the biotin molecules in the presence of small spherical Ag nanoparticles was the driving force behind the formation of the fiber-like network. This method can be effectively used for the efficient size confinement of nanoparticles in the presence of other vitamins. Such type of novel composite biomaterials can be used in high technology applications.

In another variation of Ag-Biotin system, Ag nanoparticles have been prepared by photo-reduction of AgClO₄ with monochromatic (253.7 nm) UV irradiation in the presence of biotin and benzophenone (BP). It has been shown that in the formation and stabilization of Ag nanoparticles, biotin (vitamin H) plays a significant role. Laser flash photolysis experiments were carried out to study the mechanism of formation of Ag nanoparticles.

There have been very few reports, where ligands have been utilized for the stabilization of different shapes of metal nanoparticles. Ag nanoparticles are being used as biological sensors, in drug delivery systems and as potential bactericidal agents. Ethylene glycol-bis(2-aminoethyl ether)-N,N,N′,N′-tetraacetic acid (EGTA) forms strong chelates with many di- and trivalent cations and is widely used in biological science. In this work, we report the effect of ethylene glycol-bis(2-aminoethyl ether)-N,N,N′,N′-tetraacetic acid (EGTA) in the formation of different shape of Ag nanoparticles by utilizing the complexation properties of EGTA with the Ag ions. For the formation of different shapes of nanoparticles, initial nuclei play an important role.
due to which the growth of the particles takes place. The silver nanoparticles prepared by \(\gamma\)-irradiation in the presence of EGTA showed the presence of large spherical aggregates as well as triangular nanoplates of 500 – 700 nm. Pulse radiolysis results showed that EGTA stabilizes initial clusters of silver. Time dependent UV-Visible and ATR-FTIR studies showed the adsorption of EGTA on the initial Ag clusters as well as the Ag nanoparticles. It appears that as the synthetic method changes, the role played by EGTA in the formation and growth of silver nanoparticles varies thereby leading to the formation of different shape of nanoparticles.

Anionic surface stabilization is in itself a whole new area of surface chemistry. Anions stabilize the metal nanoparticle surface by electrostatic stabilization. Keggin anions \([\text{X} \text{M}_{12} \text{O}_{40}]^{(8-n)^-}\) are a subset of polyoxometalates and are receiving increasing interest in material science, catalysis, biology and medicine owing to their chemical, structural and electronic versatility. They are able to act as electron relays, where a systematic electron transfer to the respective metal salt can give metal nanoparticles. These Keggin ions can undergo stepwise multi electron redox processes without undergoing a structural change. They may be reduced electrolytically, photochemically and also with suitable chemical reducing agents. In this report we put forward a new dimension to the synthesis of metal nanoparticles by the use of Keggin anions as reducing as well as capping agent in an attempt to synthesize gold nanoparticles of different shapes. Probably, this is the first report where a biologically important inorganic molecule like heteropolyanion has been used for the reduction, stabilization as well as a template for shape control of gold nanoparticles. Two different Keggin anions \(\text{PW}_{12} \text{O}_{40}^{3^-}\) and \(\text{SiW}_{12} \text{O}_{40}^{3^-}\) have been used for the reduction and subsequent stabilization of the gold nanoparticles. The formation of colloidal gold solution was monitored using UV-visible spectroscopy. The results of these studies showed that the concentration of Keggin anion is an important factor to control the morphology of the gold nanoparticles.

Polyoxoanions having discrete structures are of interest for pharmaceutical applications also (e.g., antiviral, -cancer, -tumor). Such properties can be improved by modifying the polyoxometalate core structure. Derivatization of the polyoxometalate has been one of the common methods of attaching important organic groups to the surface of the polyoxoanion. One such organic compound having potential applications in pharmaceuticals is thiourea. Antiviral properties of certain thiourea derivatives have

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been reported in which the antiviral effect has been attributed to the presence of the stable NHC(=S)NH grouping. With new technologies like drug delivery, exciting possibilities for anchoring metal nanoparticles over such biologically important compounds could lead to improved control over diseases. For example, metal nanoparticles in particular have exhibited tremendous potential for detecting fragments of viruses, pre-cancerous cells, and as disease markers, and indicators of radiation damage. In view of such importance, in the present work, gold nanoparticles of different sizes anchored over thiourea derivatized polyoxometalate have been prepared in DMF solvent by UV irradiation. Seed mediated growth method has been used for the preparation of larger gold nanoparticles. The polyoxometalate acts as a photochromic reducing agent as well as an efficient stabilizer for the gold nanoparticles.

Regularly ordered 1D, 2D and 3D superlattices of metal nanoparticles have vast applications for optical devices such as antireflective surface coatings, optical gratings, solar absorbers, and SERS. Hydrophobic compounds such as alkanethiols, alkylamines or cationic surfactants have been used to drive the nanoparticles towards self-organization in to such superlattices. Hence nature of the thiol ligand used plays an important role. One such thiol terminated bulky ligand is the thiol functionalized polyoxometalate. The length and the nature of the other end of the thiol molecule play an important role. Although numerous studies deal with hybrids including polyoxometalate only a few describe the preparation of hybrids containing thiol groups and the use of such hybrids for the synthesis of metal nanoparticles. In this work we report the radiolytic synthesis of gold nanoparticles passivated by γ-[SiW_{10}O_{36}(HSC_3H_6Si)_2O]^{1+} i.e. ([POM(SH)_2])^{1+} and the formation of gold nanoparticle superlattices in various ratios of DMF/water in the solution. This work demonstrates that spherical monodisperse gold nanoparticles passivated by thiol derivatized polyoxometalate ([POM(SH)_2])^{1+} synthesized by radiation induced method can self organize into various shapes of superlattices including hexagonal, cubic and icosahedral. The composition of the solvent mixture of DMF and water plays a crucial role in the formation of these superlattices.

Functional groups such as thiols and amines alone or anchored on bulky anions stabilize metal nanoparticles and limit nanoparticle growth by passivating dangling bonds. However, using the same concept to stabilize metal nanoparticles in non-polar...
solvents has often encountered stability problems. The use of giant hydrophobic stabilizing ligand like polyoxometalate (POM) in organic solvents might be a promising solution to this problem. Other alternative would be to phase transfer metallic nanoparticles into other solvents to facilitate the dispersion of particles in different physicochemical environments. Although, ingenious ways have been developed to affect the phase transfer at the interface, most of the methods are laden with their own disadvantages. In this regard a glaring lacuna has been the development of one simple nanoparticle surface capping procedure that leads to the stabilization of the metal nanoparticles in both polar and non-polar environment. Therefore, new methods for phase transfer of metal nanoparticles are endeavored.

The other current interest is to make films of nanoparticles. Recently, liquid-liquid interfaces have been exploited for the preparation of thin films, as interface between immiscible liquids is known to be ideal for assembling colloidal particles. What makes the interface unique is the asymmetry in forces that is experienced by molecules and atomic species located there together with the almost two dimensional geometry of the interface.

It is known that MELLFs, standing for metal liquid like films, are systems of highly concentrated metal colloid films separating two immiscible liquid phases. MELLFs are special cases of interfacial colloids, that is, colloids confined to the liquid-liquid interface or to the gas-liquid interface. Surfactants are known to be of importance in MELLFs. Surfactants with an anion and cation headgroups promote the formation of MELLFs. It was observed that \([\text{POM(SH)}_2]^+\) is sparingly soluble in water. Thus the presence of water might affect the stability of the Au nanoparticles attached to \([\text{POM(SH)}_2]^+\) in DMF/water solution. Moreover, a “push-pull” type of interaction might change the morphology and/or stability of nanoparticles in this solution. With this idea, we have made an attempt to exploit this phenomenon to prepare films of Au nanoparticles.

In our work, we have attempted to exploit liquid-liquid interface of different polarity instead of commonly used aqueous/non-polar (polar /non polar) interface. This method is useful to cast metal nanoparticles into a film in-situ. For this purpose, we have used two immiscible liquids (of different polarity), cyclohexane and \(N,N'\)-
dimethylformamide. We have used thiol functionalized polyoxometalates, γ-
\[\text{SiW}_{10}\text{O}_{36}\text{(HSC}_{3}\text{H}_{6}\text{Si})_{2}\text{O}]^{\text{4}^{+}}\text{ i.e. } ([\text{POM(HS)}_{2}]^+)\), to prepare metal nanoparticles.

Prefunctionalized polyoxometalate \([\text{POM(HS)}_{2}]^+\) capped Au nanoparticles were synthesized successfully in N,N-dimethylformamide and various non-polar solvents using CTAB as a phase transfer catalyst. A novel method for transferring Au nanoparticles from DMF solution into non-polar organic solvent, cyclohexane was developed. Thiol group of \([\text{POM(HS)}_{2}]^+\) provides a capping shell around Au nanoparticles. Charge neutralization using CTAB enables concentrating the nanoparticle dispersion in cyclohexane, which is a prerequisite for transfer and for successful 3D self-assembly. The dispersed particles are stable for a long period of time. After the phase transfer, Au nanoparticles could be separated out from the cyclohexane phase in the form of a powder. The hydrophobic particles thus prepared are stable and are readily dispersed in solvents like toluene and without further surface treatment. Zeta potential measurements showed that \([\text{POM(HS)}_{2}]^+\) anchored nanoparticles were negatively charged in DMF. For comparison, we used the wet chemical method and prepared films by spontaneous assembly of passivated Au nanoparticles at the DMF – cyclohexane liquid interface. The interfacial films exhibit a red opalescence due to Au nanoparticles. Measurements indicate that nanoparticles in the interfacial film form superlattices. It is demonstrated that by changing the polarity of the matrix, the interparticle spacing can be controlled. Considering the coherence, strength and flexibility of the film it does not seem to be merely metal colloid films separating two immiscible liquid phases but form a sturdy 3D membrane-like film.

Although the synthetic method reported here does not differ fundamentally from previous studies, no other method lead to comparable results in a single step, that is, one can tune the experimental conditions to get either particles in non-polar solvent or in the form of film from the same solution. Nevertheless, it opens up a new path to prepare film of the nanoparticles as well as dispersion in non-polar solvents.

Over all in this presentation, after a brief literature survey and theoretical and experimental background for the preparation and characterization of metal nanoparticles, we have described our work in detail on Ru, Pt, Au and Ag nanoparticle
systems. We have presented results, discussions and important contributions reported for the first time as have been summarized below.

1) We have combined radiation methods with diverse type of stabilizers for the preparation of Pt, Ru, Ag and Au metal nanoparticles, all application oriented systems of current interest.

2) Radiation method for Ru-Pt colloidal metal nanoparticles was used for the first time to understand the changes that take place during the formation of Pt, Ru and Ru-Pt alloy nanoparticles on a zeolite support, the acidity of the zeolite and their mutual influence. Experimental evidence for the formation and breaking of proton-metal nanoparticle adducts and the unique product selectivity in benzonitrile hydrogenation was presented.

3) In the present study we report for the first time the formation of Ag nanoparticles in the presence of biotin, and their self-assembly into long fiber-like structures useful for high technology applications in the field of biomaterials.

4) EGTA ligand was used for the stabilization of different shapes of Ag nanoparticles. The γ-irradiation and time dependent UV-visible and ATR-FTIR spectroscopic studies showed the effect of EGTA on the growth, stabilization and morphology of silver nanoparticles.

5) In the present work, gold nanoparticles of different sizes anchored over pure and thiourea derivatized polyoxometalate anions have been prepared by radiolytic method. Probably, this is the first report where a biologically important inorganic molecule like heteropoly anion has been used for the reduction, stabilization as well as a template for shape control of gold nanoparticles.

6) This work demonstrates that spherical monodisperse gold nanoparticles passivated by thiol functionalized polyoxometalate ([POM(SH₂)₄⁺) synthesized by radiation induced methods can self organize into various shapes of superlattices including hexagonal, cubic and icosahedral. These are useful for applications such as optical devices such as antireflective surface coatings, optical gratings, solar absorbers, and SERS.
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both polar and non-polar environment. Such a method has been developed in this
study. In our work, we have attempted to exploit liquid-liquid interface of
different polarity instead of commonly used aqueous/non-polar interface. A
novel method for transferring ([POM(SH₂)]⁺⁺) passivated Au nanoparticles
from DMF solution into non-polar organic solvent cyclohexane was developed.
A phase transfer catalyst CTAB was incorporated in this system to transfer Au
nanoparticles into non-polar solvents as well as to form a film of passivated Au
nanoparticles at the DMF – cyclohexane liquid interface. It is demonstrated that
by changing the polarity of the matrix the interparticle spacing could be
controlled. Considering the coherence, strength and flexibility of the film it does
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