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A strategy for the design of heterometallic oxide nanoparticle via soft chemical approach

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Outline:

Introduction

Hierarchical architecture was designed by Nature with the help of hard and soft materials to get multifunctional properties within a nanosystem. Man and material science lives in a symbiotic relationship and change their life style with time. The precise control over chemical composition, morphology and microstructural properties remains a challenging task for the scientists and engineers for the synthesis of cost effective functional nanomaterials at the bench level and then processing it at a large scale for technology use [1-15]. Novel colloidal materials with unique multifunctional properties have attracted an increasing interest because of their scientific and potential technological use with their size effects, surface defects and its interface properties during nucleation. The synthesis–structure–properties relationship with accurate stoichiometric ratio is poorly understood in bimetallic oxide nanoparticle [13-17]. With metal alkoxide, it is easy to control the nano-functional properties such as homogenous distribution, phase purity with controlled aggregation by understanding the mechanistic approach during growth process as illustrated in Figure 6.1. Metal alkoxides when used as a single source precursor (SSP) controls the chemical condensation with required stiochiometric ratio, geometric, electronic-surface morphology to design a ultra-pure functional nanomaterials [16-17].The M-O-C bond polarities, size and shape of the alkyl group, atomic radius, coordination number of the metal and the polarization degree govern the solubility and volatility parameters in molecular precursors [18-23]. Metal ion plays a critical role due to their coordination behavior to control chemical- functional properties, nucleation, growth, orientation, and formation of nanostructure by tuning surface–morphology with high performance [24-46]. Table 6.1 highlight co-relation between microscopic and nanosized parameters. With the help of soft–chemical approach the synthesis of nanoparticles takes place in two steps: nucleation processing and followed by Oswald ripening process. In nucleation process, the seeding depends on the surface energy of each particle in shaping the particle size with manipulation of thermodynamic and kinetic parameters.

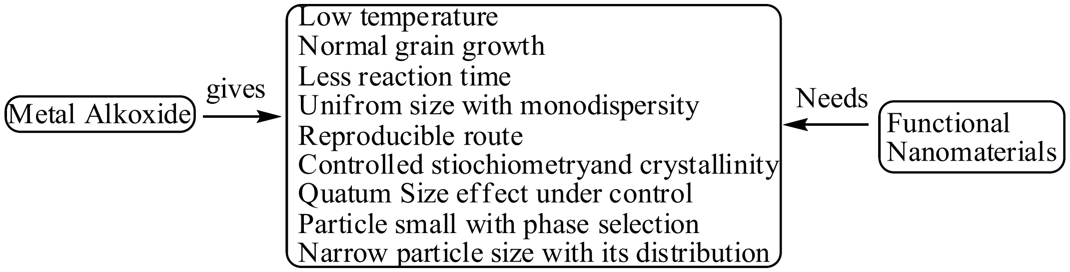


FIGURE 6.1
Unique properties can be obtained with the help of Metal Alkoxide based on Ionization potential, electro negativity and electron affinity of the metal ion

The soft–chemical approach is a flexible, simple and novel synthesis for industrial production. However with the use of different types of precursor unique features can be charged in the structural framework that affect the physical and chemical properties in the final product by retaining the stoichiometric ratio under control which help to predict favorable morphology for its futuristic applications with high reliability, accuracy and reproducible results via assembling the nanoblock in a controlled architecture framework [47-56].

TABLE 6.1
Variable parameters relationship

Microscopic parameter	Nano-sized parameters
Chemical composition	Static ,size and shape with limited aggregation
Molar ratio, pH, Ionic strength	Dynamic interaction, rate and type of precursor
Synthetic methodology	Homogenous dispersion
Ageing time	Effective inter-intra attraction forces

Theme

The size of the metal ion, choice of solvents, synthetic methodology and the temperature plays an important role to design functional nanomaterial with improved structural and morphological properties. The molecular precursor is a high fertile ground on which new multidimensional materials can be harvested by innovative routes to tailor the physic-chemical properties in molecular precursors with the tuning in chelating ligands [20-24].The efficiency of nanodevices depends on molecular homogeneity, surface-morphological properties and chemical composition in nanomaterials. Appropriate molecular precursors was focused which can guarantees a homogenous dispersion of the metal source at the molecular level with uniform reaction sites and transform it into the integrated materials with required stoichiometric ratio to generate a favorable novel properties with high precision. A pre-existent nature of metal–oxygen-ligand connectivity or by replacing the alkoxy group with chelating group helps to lowers the nucleation barrier with the formation of hydroxyl based metal alkoxides towards the synthesis of nanomaterials with crystalline phases at relatively low temperatures with enhanced functional properties. Lewis acidic behavior of the central metal ion plays an important role in moderating the physico-chemical, structural and mechanical properties of neutral organic ligands by fine-tuning the chelating ligands [18-23, 51-62]. Synthesis and characterizations of molecular precursor plays an important role to understand the particle chemistry with new horizon and offers new opportunities by understanding the structural-functional–surface properties relationship with chemical and thermal stability [41-46] to design nanodevices with high performance and reproducible results based on oxidation state of metal ion along with electro negativity, ionization potential and as well as steric factor in the chelating group. Aim and objective of the chapter has been illustrated as shown in Figure 6.2.

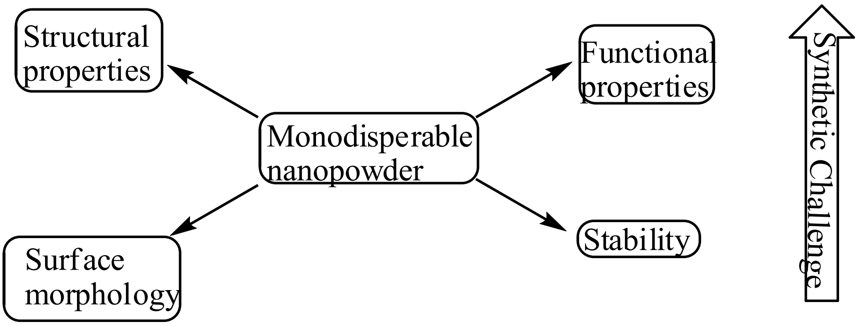


FIGURE 6.2 A Profile of synthetic chanllenge in heterometallic oxide nanopowder

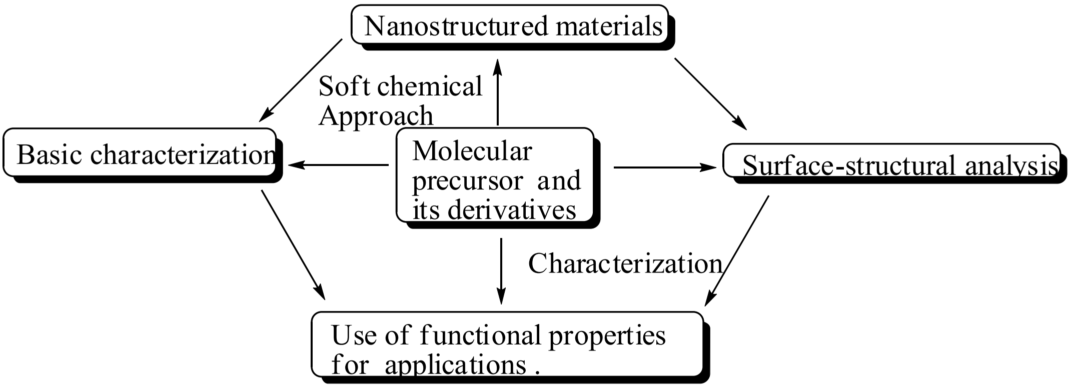


FIGURE 6.2
Aims and Objective of the chapter

Chemistry of Metal Alkoxide

Chemical aspects help to study and control soft chemical approach with hydrolysis and condensation reactions which depends on the electronegativity of the metal ions. The chemistry of heterometallic alkoxide remains insufficiently explored in nanoscience. With the easy control over reaction kinetics with better match between molecular precursors and its metal oxide remains a challenge. Metal alkoxides are very good single source molecular precursor (SSP) due to its high reactivity which depends on the electronegativity of the metal ion ,ability to increase the coordination numbers ,the steric hinderance in the alkoxy groups and with molecular structure help for the synthesis of corresponding colloidal metal oxides with high homogeneity. The presence of metal ion plays a critical role due to their coordination behavior for controlling a chemical functional behavior, nucleation, growth, orientation and formation of nanostructure material with high performance with the help of tuning the surface–morphology.

The presence of M-O-C bond polarities, size and shape of the alkyl group, atomic radius, coordination number of the metal and the degree of polarization govern the solubility and volatility as a prime requirement for better understanding the transformation of molecular precursors into nanomaterials.

The metal alkoxides were charged with low degree of electron donation from the alkoxo-oxygen to the central metal to gives monomeric precursor [18-50]. The properties of molecule can be coded with the help of structural framework which depends with chemical environment around the central metal ion. The heterometallic oxide material was synthesized by cost effective wet chemistry with required functional properties at moderate temperature to give high crystalline nanostructure powder in good yield by balancing thermodynamic –kinetic parameters. The formation of crystalline nanostructure can be adjusted with the help of growth process and minimum reaction time as highlighted in Figure 6.3.

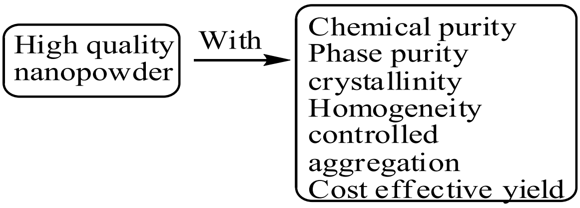


FIGURE 6.3
The syngeric relationship between nanopowder with surface chemistry for controlling the particle properties

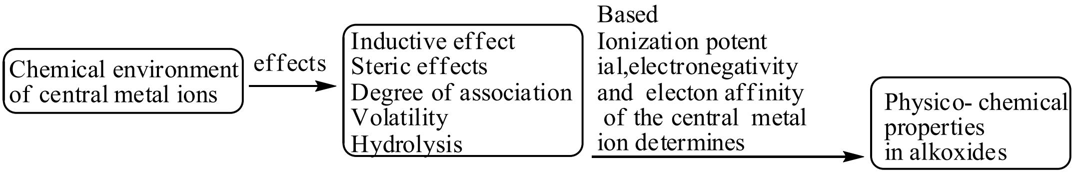


FIGURE 6.4
The co-relation between the central metal ion for controlling the physico-chemical properties

The synthesis of single source precursor (SSP) was carried out based on Molecular Structure Design concept (MSDC) for the stabilization via transformation into a solid crystalline structure. Formation of metal alkoxide takes place when hydroxyl hydrogen of an alcohol is replaced by a metal cation. In general the primary and secondary alcohols have a strong tendency towards polymerization to form coordinating polymers by increasing the coordination behavior to give novel properties with new reactivity based on electronic and steric demands of alkoxy groups as shown in Figure 6.4 [18-38]. Heterometallic alkoxide shows different physical and chemical properties due to the presence of two different types of metal ions which act as Lewis acid with alkoxy group and it is a driving force for self-agglomeration. The physic-chemical properties of bimetallic alkoxides can be explained with the help of inductive and steric effects, degree of polymerization, volatility as well as the alcoholysis and hydrolysis reactions which help in structural elucidation [64-68]. The degree of association increases with coordination behavior, which depends on type of solvent used and steric bulk in alkoxy groups [18-23]. The presence of Lewis acids and its base shows polymeric nature, which depends upon many factors such as nature of solvent used, steric factors of the alkoxide group, nature of metal ions and its coordination numbers. The stability of heterometallic alkoxide depends with the rate of crystallization and its temperature [18-47]. There is an urgent need to use simple, high stability and easily accessible alkoxy precursors to design a new ultra-pure functional nanomaterial as highlighted in Figure 6.5.

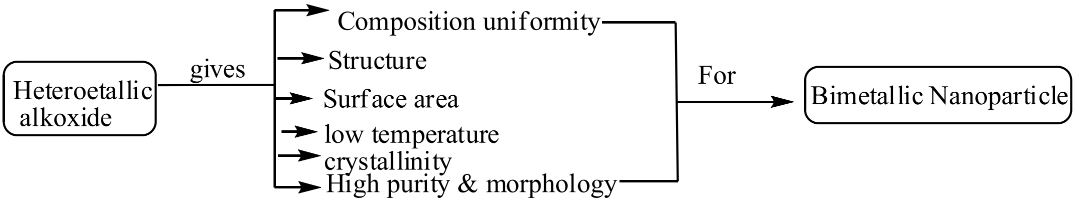


FIGURE 6.5
With the help of alkoxide purity of materials is obtained with an increased surface area and quantum effects

Based on donor-acceptor functionalisation concept both steric demands and σ donor stabilization of alkoxo ligands along with polarity, dipole moment with acidity of the solvents help to tailor the properties with reference to charge–to-radius ratio for the synthesis of monodispersable metal oxide nanopowder. The molecular precursor helps to controls the particle functional properties at the nanoscale during soft –chemical approach [32-78]. The soft chemical process is flexible, simple and novel for the preparation of homogenous, well dispersed colloidal nanomaterials at the bench scale and then processing it to a production level.

- Good solubility, volatile and stability in organic solvents depend with the nature of alkoxy ligands.
- Controlled hydrolysis gives only alcohol by replacement of alkoxy group with chelating group used.
- Good accessibility and sensitivity with moisture.
- Ability to control the composition, structural–surface property relationship.
- Ability to control the chemistry with the help of self-directed chelating groups.
- Ability to construct a new species with refined physico-chemical properties.

The formation of complexes takes place in the following two steps such as.

(1) Lewis acid–Base interaction (exploiting the difference between two or more metal atom based in electronegatively) which depends with the role of central metal ion to acts as an acceptor for the electron density and the role of ligands as a better donor.
(2) Isomorphism substitution–has a tendency to provide a homogenization at the molecular level due to its competitive π-bonding.

The intermolecular forces help to predict the physic-chemical properties in molecular precursor such as Van-der Waal interactions, π-stacking or hydrogen bonding which induces an interaction of metal ion with π donor ligands by adopting a bridging role towards their stabilization at the molecular level in attaining a higher oxidation state within a co-ordination sphere [20-23]. The change in electronegativity helps to controls the nucleophilic reactions in the synthesis of nanomaterials.

- The greater reactivity of molecular precursor requires a strict control in processing conditions.
- Intramolecular hydrogen bonding increases through alkoxy group which leads to the oligomerization by changing the coordination numbers around central metal ion with kinetic properties.
- Oligomerization depends with nature of chelating ligands to controls the chemical reactivity.
- The nature of oxygen-metal bond affects both their structural and thermodynamic properties.
- Stability, functionality and solubility changes with organic solvent for controlling the degree of polymerization with time.
- The synthesis of precursors was carried out by taking stringent precautions to avoid moisture by using

a state of the art of vacuum line. A synthesis route plays an important role to design target materials with required functional properties in the bottom to top synthetic approach.

The synthesis of nanomaterials with tunable size and long term stability remains a challenge .By using new single source precursor (SSP) by tuning the strong metal-support interactions in the solvent system along with its concentration and annealing temperature help to design new functional properties as illustrated in figure 6.6 and table 6.1 [54-87]. The preparation involves the chemical transformation of molecular precursor into well –defined metal oxide network with high crystalline structure in ionic solvent with favorable particle properties at moderate temperature.

1. The synthesis and characterization of metal alkoxides among d and p type orbital and its conversion into corresponding metal oxide nanoparticles in an environmental friendly route.

$$
\begin{aligned}
&MCl_2 + 2KM'(OR)_3 \longrightarrow 2KCl\downarrow + [M\{M'(OR)_3\}_2]\\
&[M\{M'(OR)_3\}_2] + 2M''Cl_2 \longrightarrow 4RCl\uparrow + [M\{M'M''(OR)O_2\}_2]\\
&[M\{M'(OR)_3\}_2] + 3M''Cl_2 \longrightarrow [M\{M_2'M_3''O_6\}] + 6RCl\uparrow
\end{aligned}
$$

$M = Be, Mg, Ca, Sr, M' = Co^{II}, Ni^{(II)}, Cu^{(II)}, M'' = Ge, Sn, Ba,$
$R = CH_3, C_2H_5, C_3H_7^{n,\,i}, C_4H_9^{n,\,t}.$

2. Synthesis and characterization of dumb bell shaped metal alkoxides between lanthanide and transition with main group metal

$$
\begin{aligned}
&MCl_3 + 3KM'(OR)_4 \longrightarrow 3KCl\downarrow + [M\{M'(OR)_4\}_3]\\
&[M\{M'(OR)_4\}_3] + 3M''Cl_2 \longrightarrow 6RCl\uparrow + [M\{M'M''(OR)_2O_2\}_3]\\
&[M\{M'(OR)_4\}_3] + 6M''Cl_2 \longrightarrow 12RCl\uparrow + [M\{M'M_2''O_4\}_3]
\end{aligned}
$$

$M = Ce, Er, Yb, \ M' = In, Tl, Bi, Al, Ga, \ M'' = Ni, Cu, Zn,$
$R = CH_3, C_2H_5, C_3H_7^{n,\,i}, C_4H_9^{n,\,t}.$

3. Synthesis and characterization of p ,d and f types' alkoxide and their change into metal oxides nanopowder

$$
\begin{aligned}
&MCl_2 + 2KM'(OR)_4 \longrightarrow [M\{M'(OR)_4\}_2] + 2KCl\downarrow\\
&[M\{M'(OR)_4\}_2] + 2M''Cl_2 \longrightarrow 4RCl\uparrow + [M\{M'M''(OR)_2O_2\}_2]\\
&[M\{M'(OR)_4\}_2] + 4M''Cl_2 \longrightarrow 8RCl\uparrow + [M\{M'M_2''O_4\}_2]
\end{aligned}
$$

$M = Ni, Cu, Zn, \ M' = Ce, Er, Yb, \ M'' = Ge, Sn, Sr,$
$R = CH_3, C_2H_5, C_3H_7^{n,\,i}, C_4H_9^{n,\,t}.$

4. Miscellous reactions

$$M(C_3H_7O^i)_3 + K \xrightarrow[i\text{-}C_3H_7OH]{C_6H_6} KM(C_3H_7O^i)_4$$

$$M'Cl_2 + 2\,KM(C_3H_7O^i)_4 \xrightarrow[i\text{-}C_3H_7OH]{C_6H_6} \left[M'\left\{M\,(C_3H_7O^i)_4\right\}_2\right] + 2KCl$$

$$\left[M'\left\{M\,(C_3H_7O^i)_4\right\}_2\right] \xrightarrow{H_2O} M'M_2O_4 + 4\,C_3H_7OC_3H_7$$

$M = Al, Sb, In$ $M' = Cu, Ni, Sn$ etc

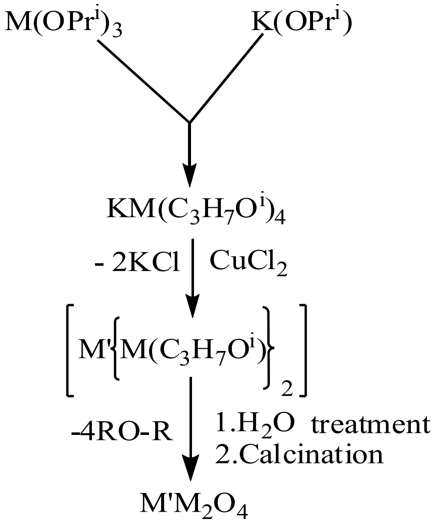
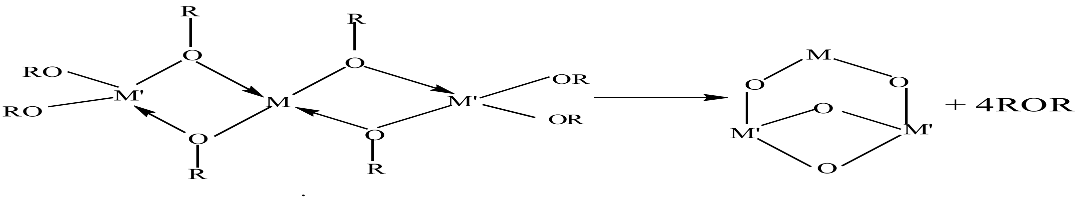
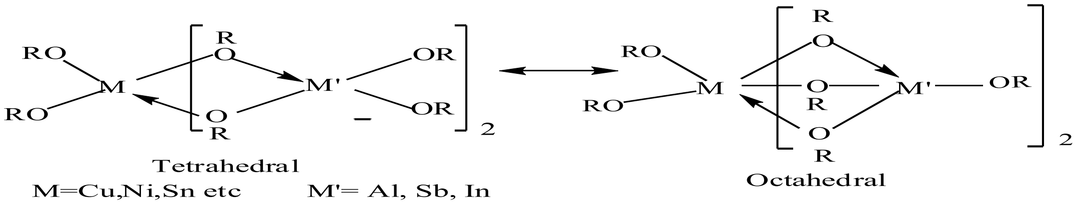


FIGURE 6.6
Flow chart for the preparation of bimetallic oxide nanoparticle



$R = C_3H_7^i$

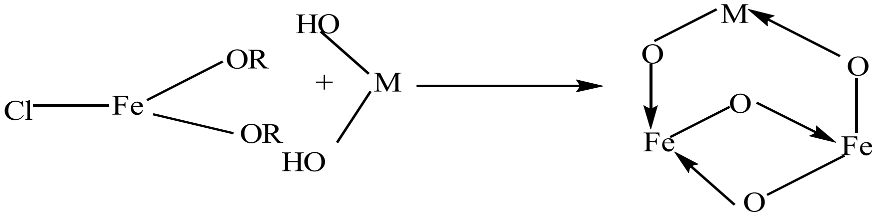
Change from Bimetallic alkoxide to bimetallic oxide nanoparticle



Equilibrium state between two structures

$$FeCl_3 + 2ROH \xrightarrow{\text{Stirring \& Heating}} ClFe(OR)_2 + 2HCl$$

$$ClFe(OR)_2 + M(OH)_2 \xrightarrow{\text{Stirring \& Heating}} M\,Fe_2O_4 + 2ROR + 2HCl$$



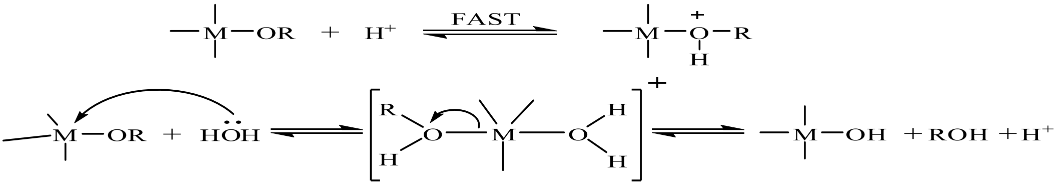
M=Mn and Co

Mechanism for the soft chemical approach

With the help of soft chemical approach, it is easy to convert alkoxy based precursors into its corresponding metal oxide framework via self –assembly with the help of hydrolysis and condensation reaction. By using SSP the homogenous size, shape, its distribution and with phase purity can be obtained by arresting the rate of aggregation by better understanding the kinetic-thermodynamic parameters in molecular species as well as the surface chemistry of the particle for its broad spectrum of applications as nanodevices.

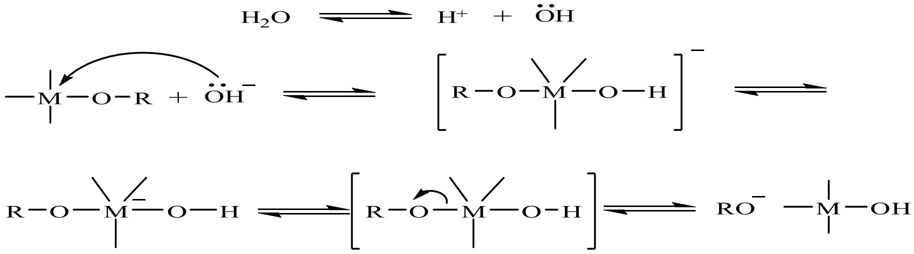
Acid –Catalyzed mechanism

The alkoxy group is protonated with electron density from metal atom with variable oxidation state to make it is more electrophilic and more susceptible for attack from atmospheric moisture which leads to the formation of metal hydroxide as transition state with the help of SN-2 type reaction.



Acid-Catalyzed Hydrolysis

Base -catalyszed mechanism:



Base-Catalyzed Hydrolysis

TABLE 6.2

Hetero metallic alkoxides are used as a potential precursor for the synthesis of mixed metal oxide nanoparticles

$MM'(OR)_6$; $M[M'(OR)_6]_2$;	$M = Li, K, Na$ $M = Mg, Ca, Sr, Ba$ $M' = Nb, Ta,$; $R = Et, Pri$
$Zn[Nb(OEt)_6]_2$ $M[M'(OR)_6]_2$;	$M = Cu, Ni, Co,$; $M' = Nb, Ta,$; $R = Me, Et, Pr^i, Bu^n$
$Cr[M'(OR)_6]_3$;	$M' = Ta$; $R = Me, Et, Pr^i$
$NaU(OEt)_6$ $M[U(OEt)_6]_n$;	$M = Ca$; $n = 2$ $M = Al$; $n = 3$
$M[M'_2(OPr^i)_9]$;	$M' = Zr$; $M = Li, Na, K$; $M' = Ti$; $M = Li$
$M[Zr_2(OR)_9]_2$	$M = Cu, Co, Ni$; $R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s$ $M = Fe, R = Pr^i$
$M[Zr_2(OPr^i)_9(OR)$;	$M = Cu, Co,$; $R = Me, Bu^s, Bu^t$ $M = Co$; $R = Pr^i, Bu^t$
$Fe[Zr_2(OPr^i)_9]_3$	
$M[Zr_2(OPr^i)_9]_2$;	$M = Ca, Ba$
$Na_2Zr_3(OPr^i)_4$;	
$MHf_2(OPr^i)_9$;	$M = Li, K$
$M[Al(OR)_4]_2$;	
$M = Be$; $R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Am^i$; $M = Mg, Ca, Sr, Ba$; $R = Et, Bu^n$; $M = Zn$; $R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Am^i$; $M = Cd, Hg$; $R = Pr^i$; $M = Co, Ni, Cu$; $R = Me, Et, Pr^n, Pr^i, Bu^n$	
$ClCo[Al(OPr^i)_4]$	
$M[M'(OPr^i)_4]_3$;	$M = Al, Ga, In$; $M' = Al, Ga$
$M[Al(OR)_4]_3$;	$M = Co$; $R = Pr^i$ $M = Cr, Mn, Fe$; $R = Me, Et, Pr^i, Bu^n, Bu^s, CEt_2Me_2, CH_2CF_3$
$Ln[Al(OPr^i)_4]_3$;	$Ln = Pr, Ce, Nd, Sm, Gd, Dy, Ho, Er, Yb, Lu, Y, Sc$
$MO_2(OAc)_2[Al(OPr^i)_4]_2$	
$(OPr^i)_{4-x}M[Al(OPr^i)_4]_x$	$M = Hf, Zr$; $X = 1,2$
$M[Al(OPr^i)_4]_4$;	$M = U$
$(OPr^i)_{5-x}M[M'(OPr^i)_4]_x$;	$M = Nb, Ta$; $X = 1, 2$; $M' = Al, Ga$
$(Ln[Zr(OPr^i)_5]_3$;	$Ln = La, Sm$
$(Ln[Zr_2(OPr^i)_9]_xCl_{3-x}$;	$Ln = La, Pr, Nd, Sm$; $X = 1, 2, 3$
$M_2Hf_3(OPr^i)_4$;	$M = Li, K$
$NaSn_2(OPr^i)_9$	
$MSn(OR)_3$;	$M = Na, K$; $R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Am^i$
$Sr[Sn(OBu)_3]_2$	
$Sb[Sn(OR)_3]_3$	$R_3 = Me, Pr^n, Pr^i, Bu^t, Am^i$
$Pb[Sb(OR)_4]_2$	$R = Me, Pr^n, Pr^i, Bu^t, Am^i$
$M[Fe(OEt)_4]_n$	$M = Li, Na, K$; $n = 1$ $M = Ba$; $n = 2$
$Ba_3Fe_2(OEt)_{12}$	
$YZr_3(OPr^i)_{15}L_3$;	$L = THF, Pr^iOH$
$YFe_2(OPr^i)_9$	
$YFe_3(OPr^i)_{12}$	
$Li_4Zn(OMe)_6$	
$Li_2Zn(OEt)_6$	
$LiZn_2(OEt)_6X$;	$X = OEt, Cl$

Chemistry of bimetallic oxide nanoparticle:

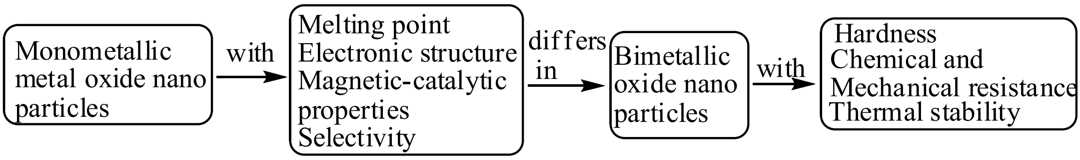


FIGURE 6.7

The change in properties between mono and bimetallic oxide nanomaterials

Economical efficiency of precursor is very important criteria for large scale production of technology grade materials with controlled size, morphology, composition, structure and surface area.

TABLE 6.3
Advantages of the soft chemical approach with other synthetic methods

Soft Chemical Approach	Chemical approach	Physical method
Well –defined and uniform crystal morphologies	Less control over crystallite size and shape	No control in shape ,size and composition
Narrow size distribution	Broad size distribution	Wide size distribution
Ultra –purity with high homogeneity and stoichiometry	Limited purity with homogeneity and stoichiometry	Non-stoichiometry and homogeneity
Low agglomeration due to control in nucleation and nuclei growth	Agglomeration not restricted due to heterogeneous nucleation and nuclei growth	Uncontrolled agglomeration and no control in nucleation and growth
Reproducible yield	Sometime reproducible yield	Non reproducible yield
Large scale production possible	Large scale production limited	Large scale production not feasible

Morphology-controlled functional properties in bimetallic oxide differs from monometallic oxide which has wide applications due to their co-relationship between structure and its physical properties as shown in figure-6.7 due to its unique mechanical, electrical, chemical and biological properties. Metal alkoxide are good and facile precursor due to the presence of pre-existing metal–oxygen units which help to form nanocrystalline oxide materials at low temperature. In heterometallic oxide the central metal ions plays a critical role to control homogeneity, stoichiometry, phase and crystallinity, which is largely depends in structure and physical- chemical properties of precursors [31-83]. The presence of two different metal atoms and its atomic distribution influences the final architectural properties with a uniform atomic distribution which help to fabricate nanodevices by controlling nucleation and growth process by restricting the thermodynamic and kinetic parameters during reactions via controlling reaction temperature, pH and types of solvent used. The advantage of soft chemical approach was discussed in Table 6.3.

Synthesis of Nanomaterials

The physical methods for synthesis of nanomaterials are cumbersome and complicated in normal conditions which takes a long times and require a high temperature resulting in a formation of heterogeneous particles, defective surface area and phase impurity as illustrated in figure-6.8. The chemistry of bimetallic oxide nanoparticles depends on particle–particle interaction with uniform size, shape and composition. In nanoparticle the solvents control the gelation time as well as morphology at the molecular level to its final material at the nanoscale. The definite particle size can be synthesized via bottom-up approach by better understanding the structure –activity relationship based on functional group. As we know the rational design of materials with controlled methodology requires a precise knowledge of structural morphology and composition of molecular precursor [63-78].The fabrication of nanomaterials into its nanodevices depends on structural-physical properties as shown in figure-6.9-6.10. The chapter highlights a soft chemical synthesis of nanomaterial along with its characterization by basic understanding the Lewis acid-base characters of metal ion. With the help of soft chemical method the physic-chemical properties can be controlled with quantum size effects (QSE) by understanding the kinetic-thermodynamic stability in mild reaction conditions which will finally help to design a new technology. The precise control of stoichiometric ratio is a key factor in tuning the functional properties for miniaturization the particle topology and also with well defined structural properties at the nanoscale [63-89].By controlling the thermodynamic parameters the nucleation, growth and aging process can be manipulated to yield nanostructured materials via self-assembly of ionic structure with required porosity, morphology, size and orientation via controlling the chemical and electrostatic forces.

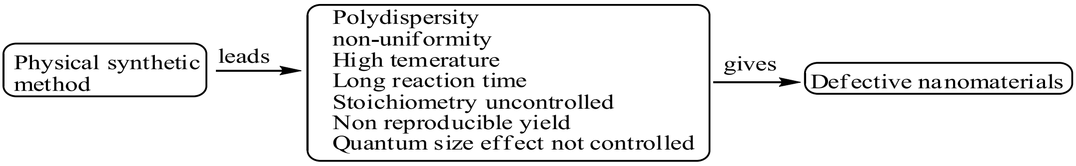


FIGURE 6.8
Drawback of the physical methods

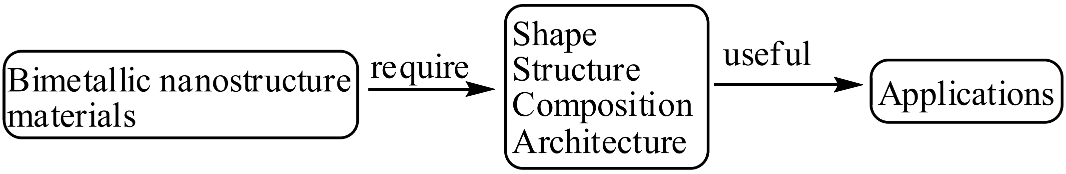


FIGURE 6.9
Successful use of nanoparticle depends above mentioned properties

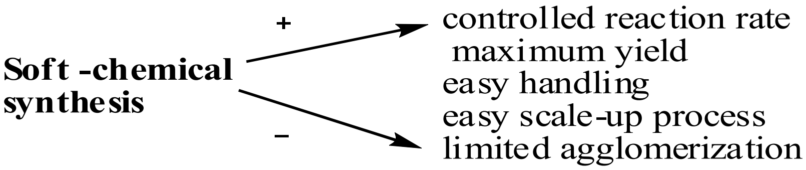


FIGURE 6.10 A
Advantages of soft chemical approach

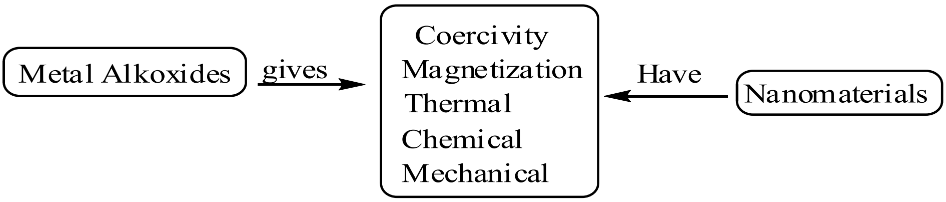


FIGURE 6.10 B
Unique properties can be controlled with the help of controlled Synthesis

The pragmatic balance highlights the challenge both in terms of present and futuristic goals and helps to establish a new technical pathway which leads to a sharp edge in technology and its utility via better understanding a synthetic methodology at the bench scales to scale up for their production scale. The correlation between precursor and synthetic methodology has been highlighted in figure 6.11 to 6.13.

Physico-chemical properties of Bimetallic Alkoxides help to change to nanostructured materials into nanodevices

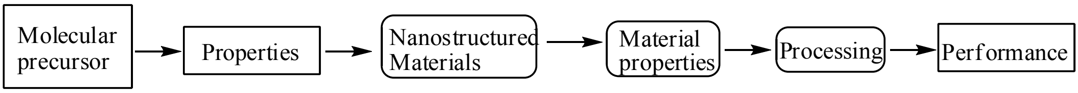


FIGURE 6.11
These components highlights their inter relationship which helps to control properties for their successful use

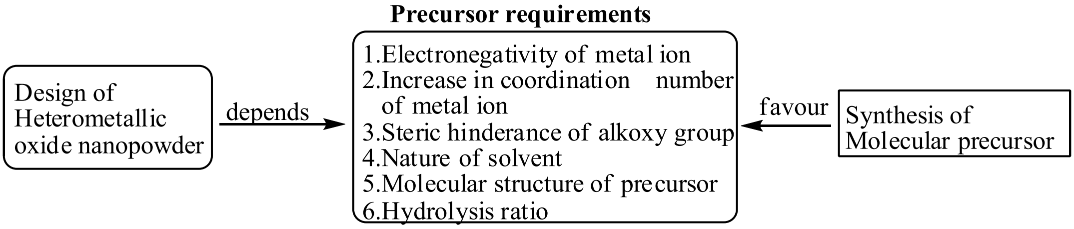


FIGURE 6.12
The co relationship between nanopowder and precursor via chemie douce approach

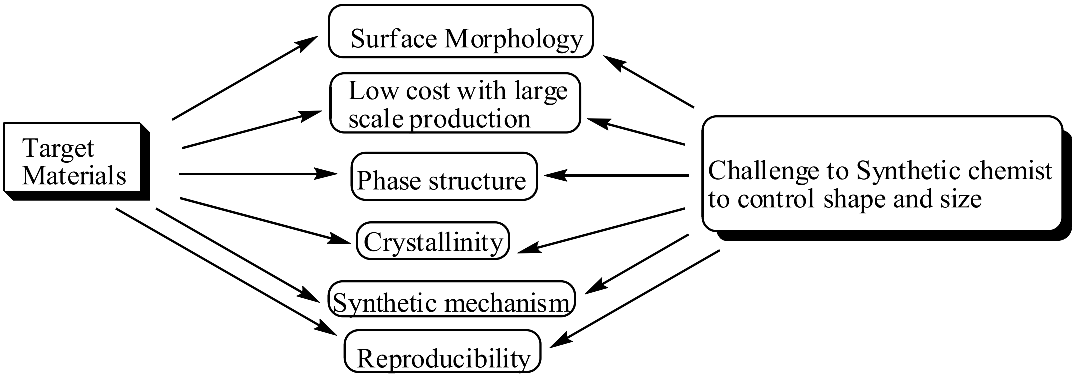


FIGURE 6.13 A
A Challenge to synthetic chemists to design a target materials

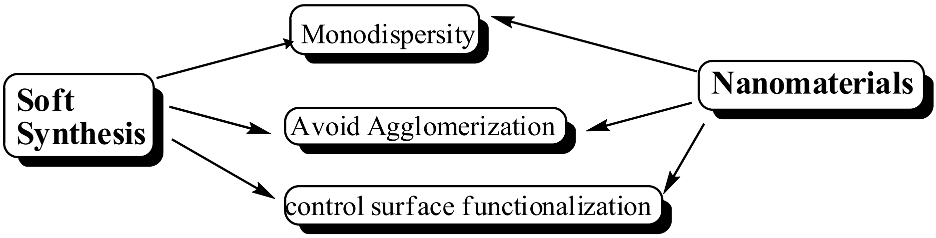


FIGURE 6.13 B
Factors for controlling the shape and size based on surface morphology

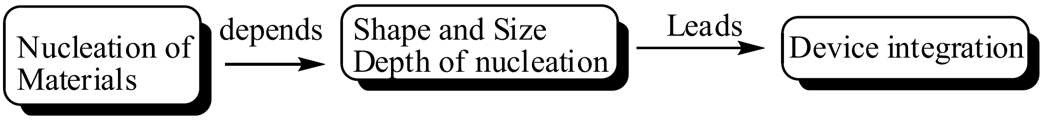


FIGURE 6.13 C
Synthesis controls size and shape in nanoparticle for functional properties

To understand the control in particle size needs a better understanding with their experimental surface conditions to design a correct functional particle as illustrated in figure-6.14-6.15 and Table 6.4 is still an open challenge to the synthetic chemists.

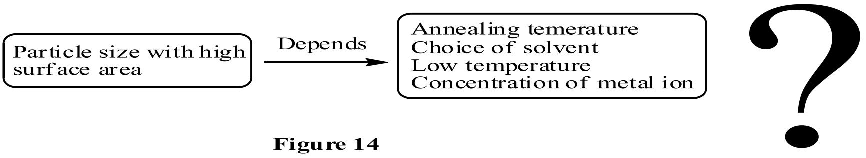


Figure 14

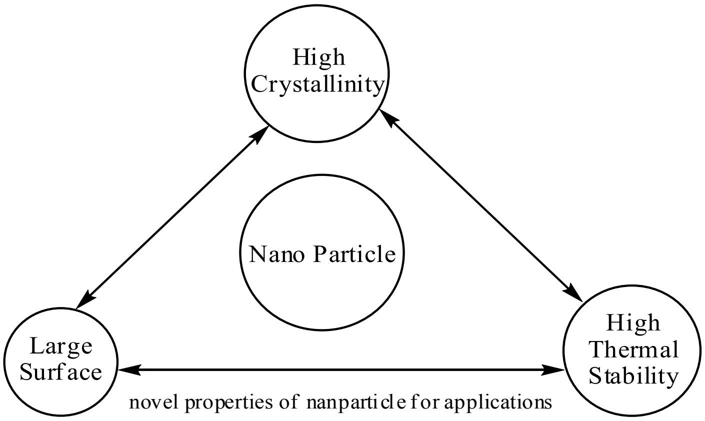
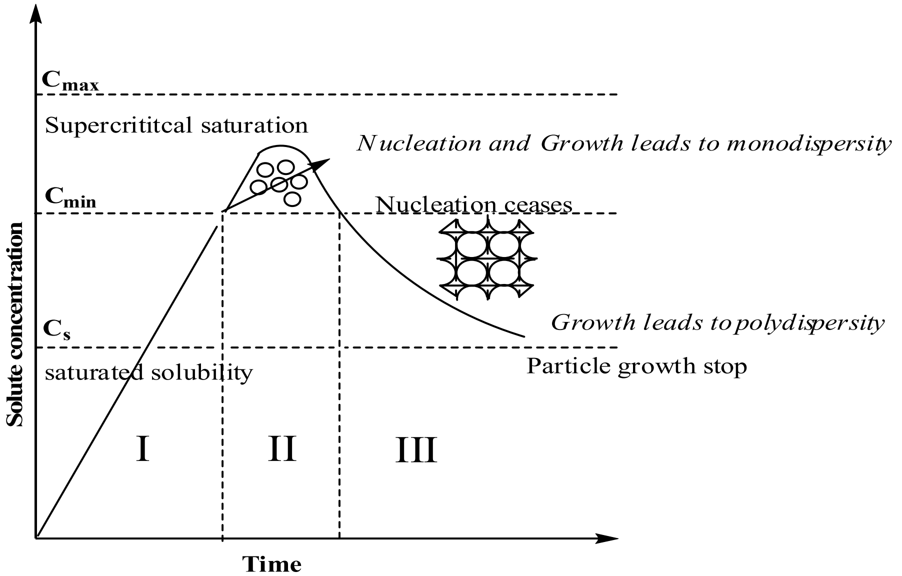


FIGURE 6.15

TABLE 6.4
Methods based on wet chemistry:

Methods	Advantages	Disadvantages
Sol gel	(a) Large scale up area (b) precise control on composition (c) Low temperature is required (d) High homogeneity with desired Surface properties (e) Simple process treatment	(a)Sensitive towards atmospheric condition (b) Raw material Expensive (c) Sometime Toxic solvent are used (d) Limited to bench level
Hydrothermal Synthesis	(a) No heat treatment is required (b) Less energy consumption (c) No milling process with less impurities (d) Complex chemical composition is obtained (e) Controlled particle size and shape (f) Cheap raw material (g) Environmental benign (h) Large scale industrial production	(a) Aggregation Rate is high (b) Chemical contamination occurs due to combustion (c) High cost equipment (d) Stringent safety precaution are required
Solvothermal Synthesis	(a) Narrow particle sized distribution (b) Monolayer ligand coating required (c) Absence of aggregation in polymer matrix (d) Crystallization rate is very high	(a) Difficult for mass production (b) High cost (c) Complicated processing treatment



Once nucleation starts the progress of growth takes place as illustrated in the figure-16

FIGURE 6.16

Figure 6.16 shows the general kinetics process takes place in three stages. In stage **I**, the concentration of precursor increases with time. With saturated conditions, the precipitation of materials fails to take place due to the energy barrier at the nucleation stage. In stage **II** (when nucleation occurs), the degree of super saturation increases to overcome the energy barrier which leads to the formation of stable nuclei. In the last stage, the nucleation is effectively stopped due to the reduction of reactant concentration, and the particles continue to grow as long as the solution remains supersaturated. The supersaturated solution is thermodynamically unstable resulting with the formation of particles nuclei during nucleation with small size and monodispersity with required shape. The materials formation and its crystallization depend on the steric profile of the organic ligands, which is controlled by the hydrolysis and condensations.

TABLE 6.5
Synthesis of metal oxide nanoparticle [63-79]

Molecular Precursor	Nano Metal Oxides
$Er\{Al(OPr^i)_4\}_3$	Er^{3+} doped SiO_2-Al_2O_3
$Er\{Ti(OPr^i)_5\}_3$	Er^{3+} doped SiO_2-TiO_2
$Er\{Si(OR)_5\}_3$	$Er_6Si_3O_{15}$
$Er\{Si(OR')_5\}_3$	$Er_6Si_3O_{15}$
$Er\{As(OR)_4\}_3$	$Er_5As_3O_{12}$
$Er\{As(OR')_4\}_3$	$Er_5As_3O_{12}$
$Er\{Sb(OR)_4\}_3$	$Er_5Sb_3O_{12}$
$Er\{Sb(OR')_4\}_3$	$Er_5Sb_3O_{12}$
$Er\{Ti(OR)_5\}_3$	$Er_6Ti_3O_{15}$
$Er\{Zr(OR)_5\}_3$	$Er_6Zr_3O_{15}$
$Er\{Yb(OR'')_4\}_3$	$Er_5Yb_3O_{12}$
$Er(OR'')_4P(OR'')_2$	
$Er(OR'')_4P\{Yb(OR'')_4\}_2$	
$Ce\{Sb(OPr^i)_4\}_3$	$Ce_5Sb_3O_{13}$
$Ce\{Ti(OPr^i)_5\}_3$	$Ce_6Ti_3O_{15}$
$Ce\{Sn(OPr^i)_5\}_3$	$Ce_6Sn_3O_{15}$
$Er\{Zr(OPr^i)_5\}_3$	$Er_6Zr_3O_{15}$
$Er\{Al(OPr^i)_4\}_3$	$Er_5Al_3O_{12}$
$Er\{Ti(OPr^i)_5\}_3$	$Er_6Ti_3O_{15}$
$Cu\{Al(OPr^i)_4\}_2$	$CuAl_2O_4$ Unpublished
$Ni\{Sb(OPr^i)_4\}_2$	$NiSb_2O_4$ Unpublished

Where: $R=CH_2CF_3$, $R'=CH_2CCl_3$, $R''=CH(CF_3)_2$

Experimental Techniques

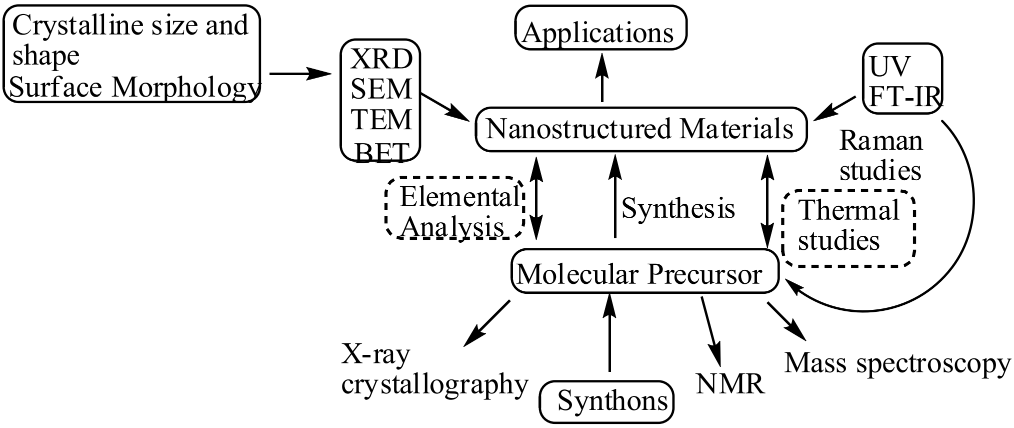


FIGURE 6.17
Graphical sketch for the techniques used for characterization

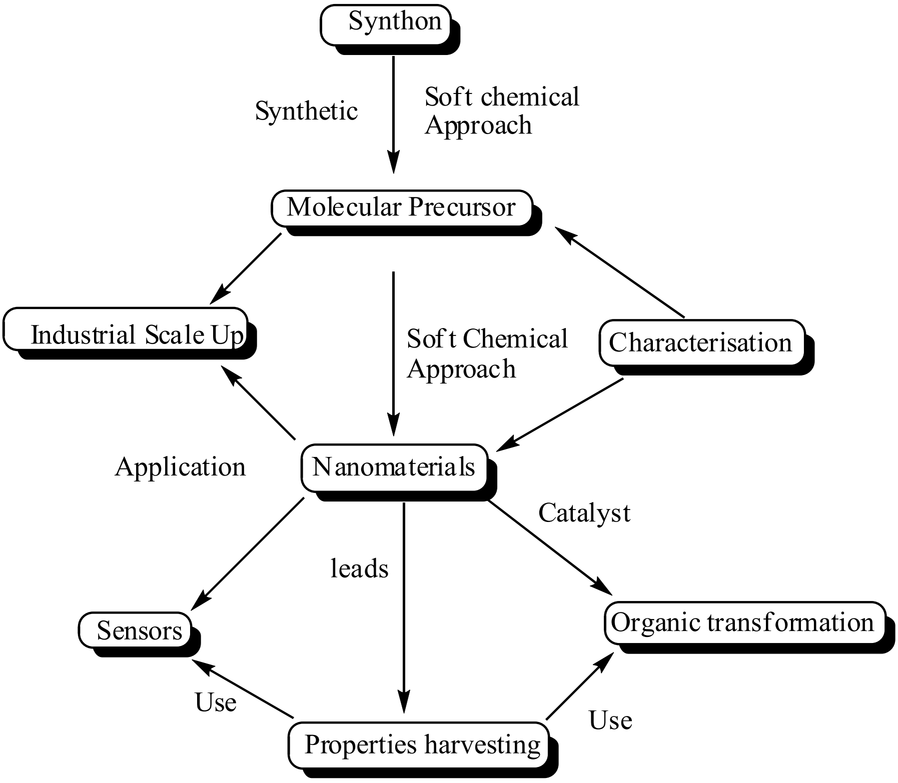


FIGURE 6.18
Graphical theme based on Chemie douce

All chemical and solvents were purified and then dried as reported in the literature [90-92]. Size ,shape and physico-chemical properties of mondisperable nanoparticles are closely related with their chemical transformations based on synthetic parameters. Many analytical approaches were studied for their structural properties at the nanoscale with their surface uniformity as well as for their bulk production via chemie –douce approach, which are as follows:

- Ionization takes place by photons and electrons followed by mass spectra for their analysis by means of quadrupole and time-of-flight mass spectrometers;
- Atomization and selection of neutral clusters takes place with respect to their masses.
- Transmission and scanning electron microscopes helps to predicts information regarding size/shape of the particles along with their distribution and topology at the nanoscale.
- Electron diffraction helps to study size and phase's structure long with their bond lengths.
- STM helps to determine the morphological properties with their surface area.
- Adsorption of gases takes place by the particle to gives information about their surface area.
- Photoelectron spectroscopy helps to determine the electronic structure of particle.
- Conductivity measurement gives information about the conduction band, percolation and topology in nanomaterials.

TABLE 6.6
Techniques used to study structural-property relationship and for its characterizations: [93-107]

Method	Properties to be analyzed
FT-IR	Vibrational stretching frequency of Metal-oxygen bond
UV – VIS Spectra	UV absorption of the amorphous gels and crystalline samples were heated at different temperatures
TG – DTA	Weight loss and thermal effects occurs during their conversion from precursors into the final metal oxides
Raman Spectra	Photons scattering and interaction with other molecule to induce Transitions with different energy levels
Mass spectroscopy	Separating the ionized species with respects to their mass
XRD	To study an extent of crystallization in the sample
BET	Accessible surface area in the particle
SEM/TEM	To study particle shape, size and morphology
Light scattering method	Particle size distribution

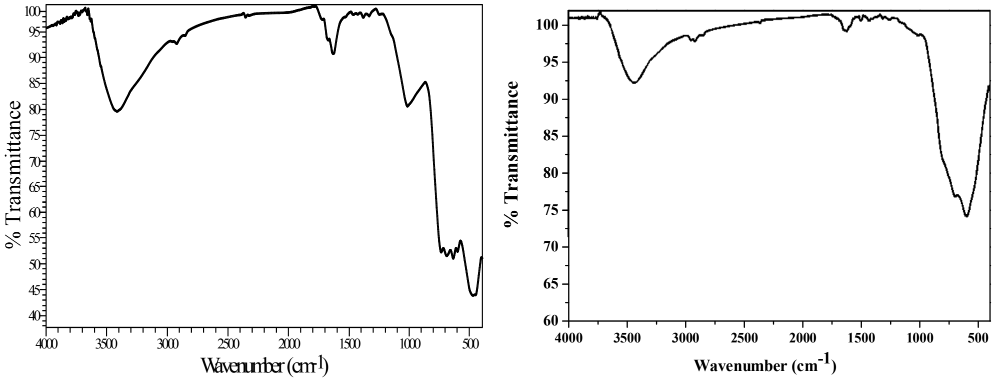
FTIR Spectra

FTIR is an important technique used for identifying different types of chemical bonds present in a molecule, by producing an infrared absorption spectrum known as a molecular "fingerprint" [95-97]. The wavelength of absorbed light is a special characteristic to their chemical bond. Molecular bonds vibrate at various frequencies which depend on the type of bonds present. According to a quantum mechanics, these frequencies correspond to the ground state (lowest frequencies) and to an excited states (higher frequencies).The increase in frequency within molecular vibration takes place with an excitation of absorbing energy .For any transition the energy must be equal to the difference between the two different states.

Difference in energy states = energy of light absorbed

The degree of absorption corresponds to the radiation at each wavelength which is quantitatively related to the number of absorbing molecules present in the sample. The linear relationship exists between the absorbance and the number of absorbing molecules, multicomponent quantative analysis of gas mixture. Infrared radiation is an electromagnetic spectrum between the visible and microwave regions in which a selection rule apply to indentify type of molecular bonds present within the molecular framework.

FT-IR shows the presence of peaks which are characteristic to the symmetric and asymmetric vibration in M-O bonds. Depending on with the type of synthetic approach the crystalline nature increases due to an intermolecular forces, which leads to the formation of self-assembled nanostructure as supported by thermal analysis and XRD studies. No change in vibration frequencies takes place even after ageing, which support the quantum size particle remains under control with no change in oxidation state of the central metal ion. The presence of stretching vibrations of OH bonds occurs due to absorption of water which takes place during the sample preparations. M-O bonds shows significant absorption peaks as well as the stretching vibration as shown in the figure 6.19.



$NiSb_2O_4$ **$Cu Al_2O_4$**

FIGURE 6.19

***Raman Spectroscopy* [93, 95]**

When photons are scattered within the molecular system it interact with other molecules to induce transitions between different energy levels. Most of the photons are elastically scattered by a process known as Rayleigh scattering .The emitted photons has the same wavelength as an absorbing photon. It is based on scattering of inelastic photons by a molecule. In Raman scattering, the energies of the incident wave length varies from 1 in 10^7 to gives photons at different frequencies due to an interaction of electromagnetic field to produce electric dipole moments. The energy for the scattered radiation is less than the incident radiation which is known as Stokes lines. The energy of scattered radiation is more than the incident radiation known as anti-Stokes lines. The change in energy from the excited state is related to the vibrational energy as spacing in the ground state thereby produces the wave number of the Stokes and AntiStokes lines which are directly related to their vibrational energies within the molecular framework.

Theory

Vibrational spectroscopy of molecules depends on quantum mechanics which requires a well-defined frequencies and atomic displacements known as the normal modes of vibrations. A linear molecule with N atoms has 3N-5 normal modes and a non-linear molecule has 3N-6 normal modes of vibrations .Several types of motions leads to normal modes .Such as 1. Stretching motion between two bonded atoms ; 2. Bending motion between three atoms are connected by two bonds; 3. Out-of plane deformation modes take place with changes from a planar structure to a non-planar one.

Specific surface area (SSA)

SSA was measured in a sorption analyzer. Samples (200 mg) were degassed at 400°C by maintaining a outgas rate 5 mm Hg/minute. An analysis was carried out at 77K with N_2. SSA was determined with the help of BET multipoint method by using at least five data points. It is used to determine the effective surface area of a solid material even with complicated shapes by using absorbed gas molecules as per rule. The average particle size was calculated with the help of following formula as shown below:

$R = \frac{3}{\rho X\,SSA}$ where R = average particle size, and ρ is the density of the material.

Mass spectroscopy

It is used for separating ionized species with respect to their masses, with their interaction between magnetic and electrical fields. Dynamic devices analyze the time taken by ions to fly at a definite distance. In mass spectrometer, separation of ions takes place in a transverse electric field, due to quadrupole capacitor constituted by the presence of 4 rods symmetric with respect to their central axis. In time-of-flight mass spectrometer, an ion packet is let into the analyzer through a grid and then “drifts” finally in an analyzer chamber then to a collector unit in such a way that heavy ion (m_1) lack behind light ions (m_2). The ion packet were separated, with respect to their same energy, while their rates and the times for flight moves along with the analyzer t which are inversely proportional to the square root of their masses: $t = L\,(m/2v)^{1/2}$, where v is the accelerating potential and L the analyzer length. The mass spectra do not give any conclusive evidence in the gas phase probably due to breakdown of the heterometallic alkoxides into simple metal alkoxides, finally breakdown into simple metal oxides under the high vacuum pressure used in mass spectrometer.

Ultraviolet and visible spectroscopy [94, 98]

Molecules absorb ultraviolet or visible light. The absorbance in a solution increases with an electronic beam which is directly proportional to their path length and with the concentration of absorbing species. Different molecules absorb radiation with different wavelength which corresponds to the structural groups within the molecular framework. When atom or molecule absorbs energy, electrons were promoted from ground state to an excited state. Electron can rotate and vibrate with respect to each other having discrete energy levels, which can be packed on the top of each electronic level.

Charge-Transfer Absorption

Inorganic species have a tendency with charge–transfer of electron which depends on the electron donating –accepting properties. Absorption of radiation takes place by involving the transfer of an electron from the donor to an orbital associated with an acceptor.

The absorption of light energy accelerates with movement of electrons in σ, σ and ñ –orbital's from the ground state to the higher energy state. According to the molecular orbital theory, the electrons were excited by the absorption of energy; from a bonding to an antibonding orbital. With different vibrational modes the electronic energy exhibits the variable frequencies.

In down field frequency shift in UV–visible absorption which supports the exponential change to take place in the crystalline structure which is co-related with an increase of band gap energy with decrease in grain size which is related to the quantum size effect and with their oxygen vacancy, which may leads to defective emission. The absorption frequencies increase linearly with an increase in photon energy.

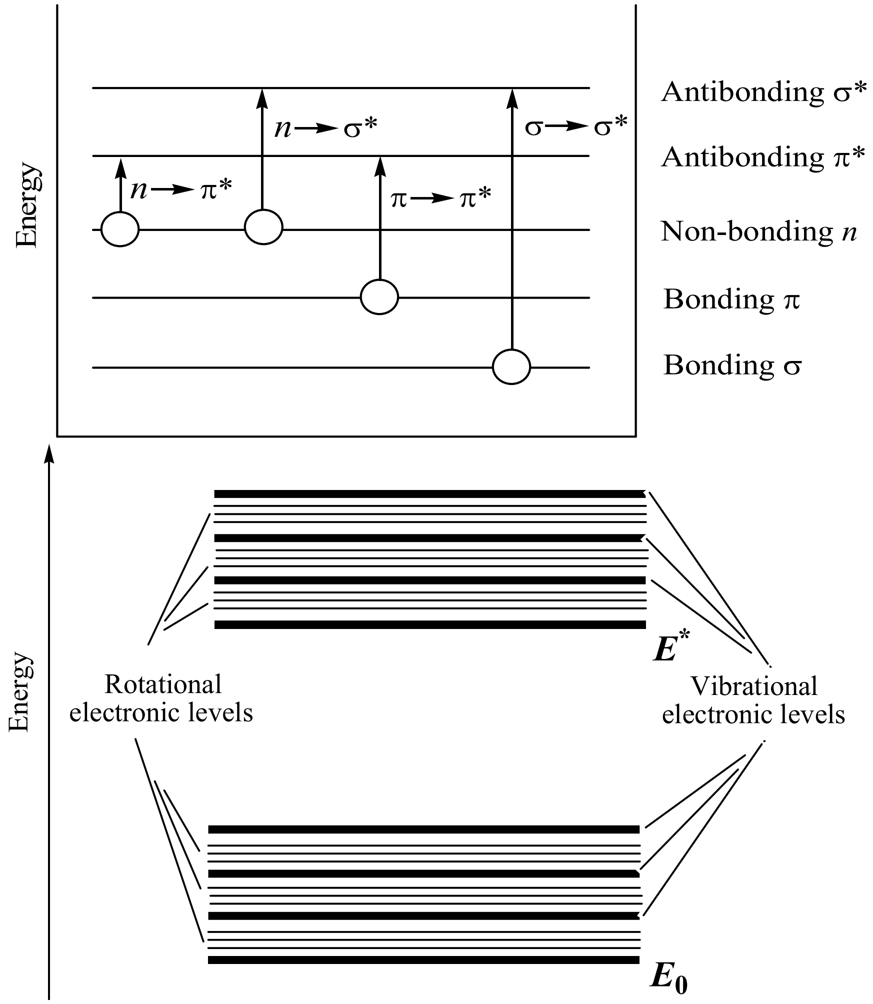


FIGURE 6.20

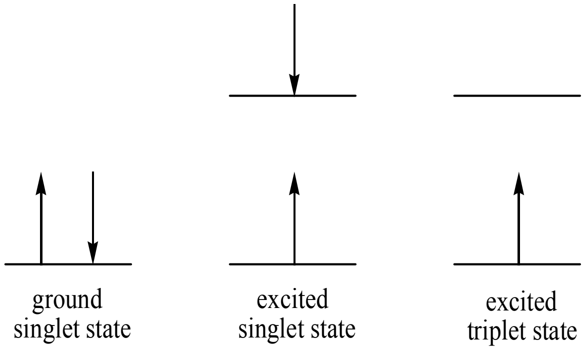
The inclination of linear curve occurs due to UV absorption for charged transition at the topmost occupied state of valence band to the bottom most unoccupied state of the conduction band. The absorption peaks corresponds to the Π-Π* transition with blue shift confirming the formation of monodispersed particle. It is clear from UV absorption, band gap increases with decrease in particle size. UV-visible spectra can be attributed to the charge transfer band of unshared electron pairs on the oxygen atoms to an empty metal orbital. The nature of metal ion helps to study a subtle changes to takes place in their coordination number and as well as oxygen donor ligands. The broadness of the emission frequencies indicates the presence of broad particle with large size distribution with low crystallinity. The fine structural peak is virtually unchanged in a solvent thereby support the presence of weak interaction within particle regime

Luminescence

The emission of light takes place when an electron returns to the ground state from an excited state and loses its excess energy as photon. Luminescence spectroscopy is related to three different techniques. Which are as follows:

- Molecular Fluorescence spectroscopy,
- Molecular phosphorescence spectroscopy
- Chemluminescence spectroscopy

Fluorescence and phosphorescence (photoluminescence spectroscopy).The electronic states in the molecules can be divided into singlet and triplet states:
Singlet state: All electrons in the molecule are spin –paired
Triplet State: One set of electron spins is unpaired



Fluorescence

Absorption of UV radiation takes place when a molecule excites from a vibrational level to an excited state, which is usually known as the first excited singlet state. An exited molecules fall to their lowest vibrational level by losing an excess energy to other molecules due to molecular collision. Fluorescence occurs when the molecule returns to the electronic ground state from an excited singlet state by emission of a photon .If a molecule absorbs UV radiation if it does not fluoresce it means losses its energy in some other form. These processes are known as radiation less *transfer of energy*.

Intra-molecular redistribution of energy between possible electronic and Vibrational states

When molecule returns to its electronic ground state .The excess energy is converted into vibrational energy (*internal conversion*), and the molecule are placed under stressed with high vibrational level. An excess vibrational energy is lost by collision with some other molecule which is known as *vibrational relaxation*. The conversion of electronic energy into vibrational energy helps to reorient itself for conversion as an internal energy.

A combination of intra and inter –molecular energy redistribution

The spin of an excited electron can be reversed, leaving the molecule to an excited *triplet* state; known as an *intersystem crossing*. Triplet state moves in a single state with an increase of energy level in vibrational modes due to collision within a solvent system. Then it undergo to a second intersystem crossing with high vibrational level at the electronic ground state .Finally, the molecule returns to the ground state by relaxation due to their low vibrational energy.

Phosphorescence

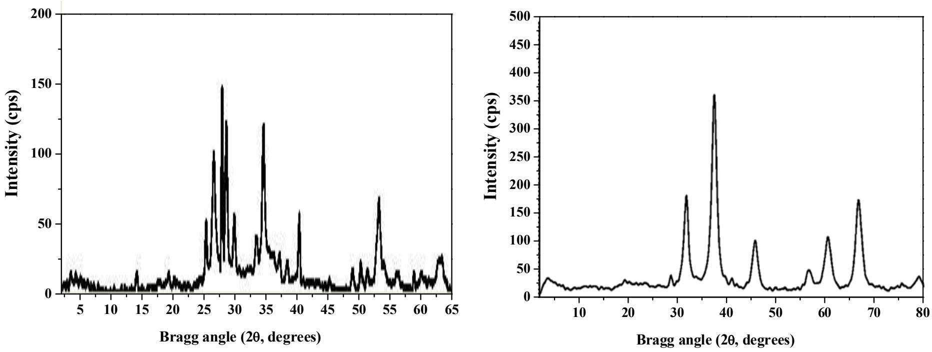
A molecule will never remains in the excited triplet state due to unstability ,due to excited state of electron and it return to the ground state by loosing extra energy by an emission of photon .A triplet /singlet transition is always less probable than a single transition. Emission from triplet/singlet state will continue even after an initial irradiation with the help of an internal conversion of energy and transfer of energy successfully as phosphorescence at low temperature.

Chemluminescence

Chemluminescence occurs when a chemical reaction produces an excited species to emit a photon in order to reach at the ground state. These reactions can be encountered within a biological system known as *bioluminescence.*

XRD Studies

XRD help to determine the structure how the atoms are packed together in the crystalline state along with their interatomic distance and angle with their wavelength to give information about the crystal lattice, structure, orientation and its particle size .The intensity of the diffracted X-rays were measured as a function of diffraction angle 2θ. With calcinations the broadness of diffraction peaks reduces due to removal of volatile impurities from the surface , thereby supports the formation of crystalline structure with correct phase, and with favorable microstructural properties. The figure 6.21 shows the information about the crystallographic structure with phase composition. By using Bragg ‘S law, the wavelength of the beam combined with parameters from the scattered X-rays gives the d-values. The d values gives the distance between the lattice planes $N\lambda= 2d\sin\theta$. With the help of Scherrer equation the crystallite dimension (D) can be calculated by using following equation $D= C\lambda/ \beta\cos\theta$ [99-102].



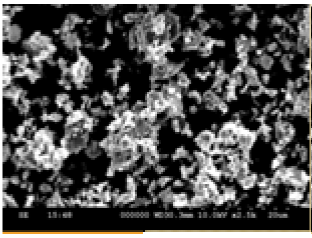
$NiSb_2O_4$ $CuAl_2O_4$

FIGURE 6.21

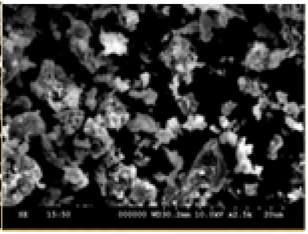
Scanning electron microscopy (SEM)

Accelerated beam of electrons carries significant amounts of kinetic energy, and then dissipated at different signals in relation to electron-sample interactions. When the incident electrons were deaccelerated in solid sample leads to generate a high resolution for studying the shapes, orientation and phase purity with crystallinity along its chemical compositions [93,103]. One disadvantage of this technique is that the sample surface should be an electrical conductivity. A field emission SEM was used to study surface morphologies of the particles. The samples were well dispersed in a distilled H_2O by using an ultrasonic horn then placed on an aluminium stub to allow drying for 4 h on a hot plate. Powders were sputter coated with 10-40 nm of Au-Pd to reduce charging effects. Operating voltage used in between 15.0 and 30.0 kV. An electron beam is constricted by magnetic lenses to give a thin (1-10 mm) probe, which travels progressively; point-to-point over a sample for scanning with an interaction of electrons with surface generates several types of emission with their conversion into an electrical signal. Electrical signals are then amplified and fed into a cathode-ray tube. Images formed on the screen were then photographed. The major advantage of this technique is to get structural information with long scanning times. The method is usually employed to study the particle size along with its distribution. With the help of histogram the extent of monodispersity can be analyzed.

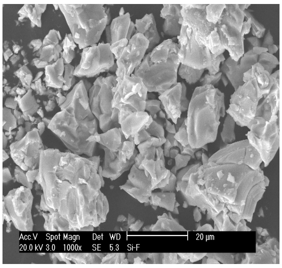
Some SEM data of bimetallic oxide as illustrated below:



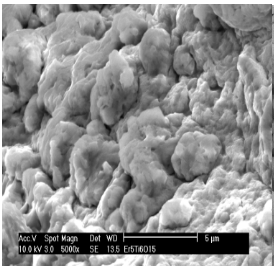
$CoFe_2O_4$



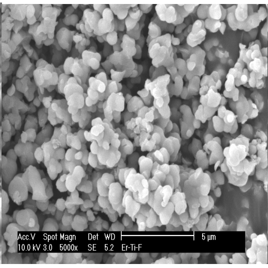
$MnFe_2O_4$



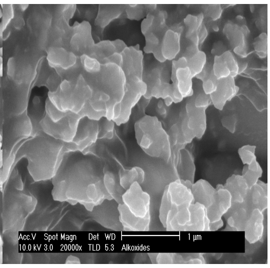
$[Er\{Si(OR)_5\}_3]$



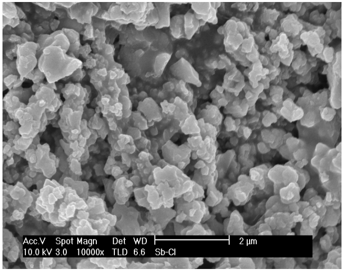
$[Er\{Sn(OR)_5\}_3]$



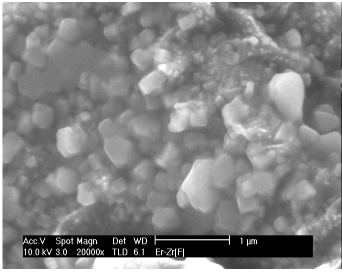
$[Er\{Ti(OR)_5\}_3]$



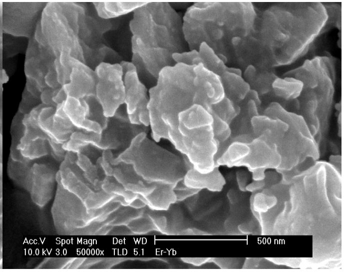
$[Er(OR'')_4P\{Yb(OR'')_4\}]_2$



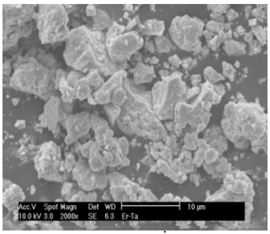
$[Er\{Sb(OR')\}_4]_3]$



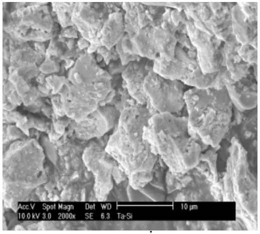
$[Er\{Zr(OR)_5\}_3]$



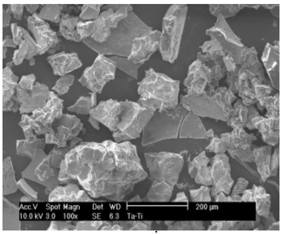
$[Er\{Yb(OR'')_4\}_3]$



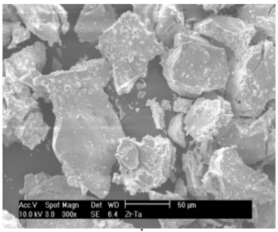
$[Er\{Ta(OPr^i)_6\}_3]$



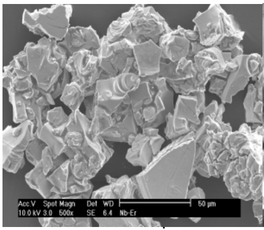
$[Er\{Ta\cdot Si(OPr^i)_2O_4\}_3]$



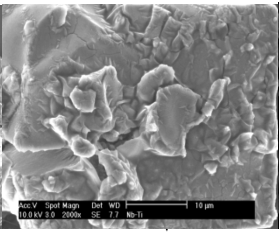
$[Er\{Ta\cdot Ti(OPr^i)_2O_4\}_3]$



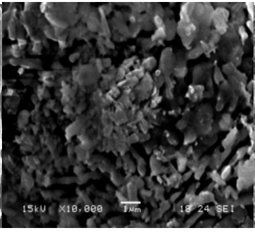
$[Er\{Ta\cdot Zr(OPr^i)_2O_4\}_3]$



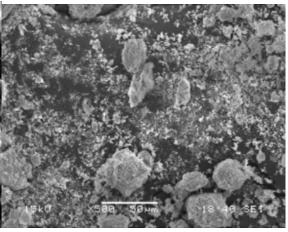
$Er\{Nb(OPr^i)_6\}_3]$



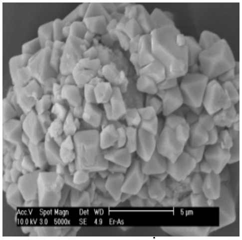
$[Er\{Nb\cdot Ti(OPr^i)_2O_4\}_3]$



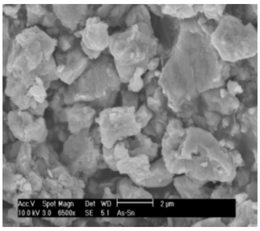
$[Er_2TiO_5]$



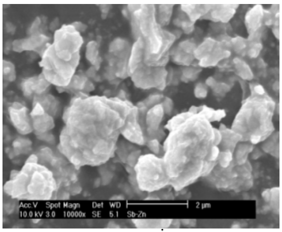
$[Er_2ZrO_5]$



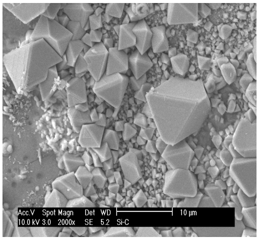
$[Er\{Si\cdot Sb(OPr^i)_2O_3\}_3]$



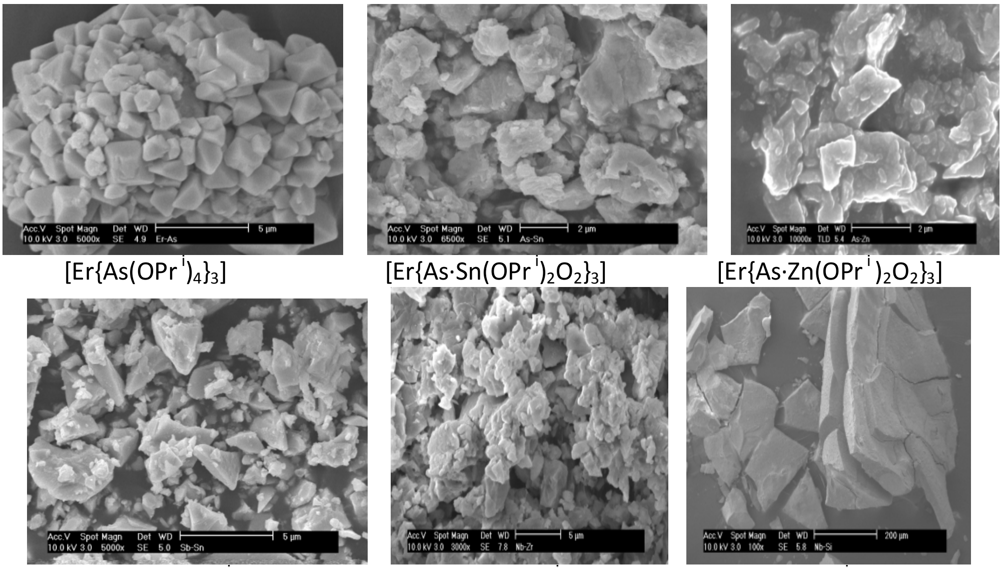
$[Er_5Al_3O_{12}]$



$[Er\{Sb\cdot Zn(OPr^i)_2O_2\}_3]$



$[Er_2SiO_5]$



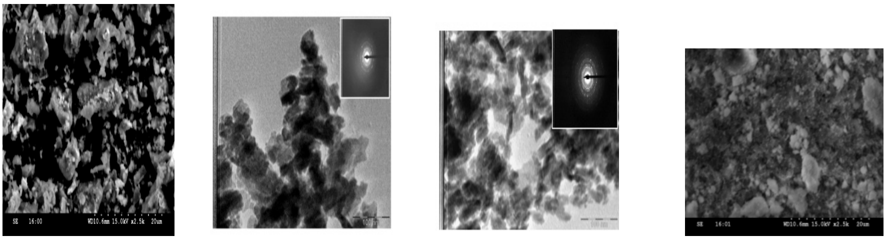
$[Er\{As(OPr^{i})_4\}_3]$ $[Er\{As{\cdot}Sn(OPr^{i})_2O_2\}_3]$ $[Er\{As{\cdot}Zn(OPr^{i})_2O_2\}_3]$

$[Er\{Sb{\cdot}Sn(OPr^{i})_2O_2\}_3]$ $[Er\{Nb{\cdot}Zr(OPr^{i})_2O_4\}_3]$ $[Er\{Nb{\cdot}Si(OPr^{i})_2O_4\}_3]$

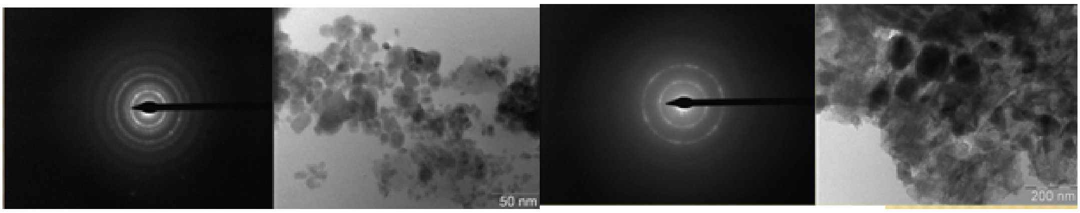
FIGURE 6.22

Transmission electron microscopy

It is an analytical technique with a high resolution used to measure the particle sizes, topography, composition as well as crystallographic information and morphologies which is based in the same principle as light microscope [93,103]. With the help of TEM it is possible to get resolution of sample in many thousand times better than with a light microscope. The samples were prepared by dipping a holey carbon grid in a vial of emulsion with as-prepared powder. The specimen was held in a Gatan double tilt goniometer with an operating voltage of 300 kV. A sample shaped as a thin film was trans-illuminated to a beam of accelerated electrons with energy level ranges from 50-200 keV in vacuum of ca. 10^{-6}mm Hg. The electrons were deflected at small angles by atoms in a sample and then passed through the sample to get into a system of magnetic lenses to form a bright-field image of an internal structure in a screen sample. A resolution of 0.1 nm was achieved, which corresponds to a magnification factor of 10^6. The resolution depends on the nature of the sample and its method of preparation to get a better diffraction patterns to provide information about the crystalline structure in high vacuum. Selected area electron diffraction (SAED) gives information for the particle size. Aggregation process takes place within particle due to the presence of weak inter-intra particle forces. During synthesis process, the coalescence of the smaller particle leads to the formation of the large crystalline nanoparticle due to active surface area. SAED shows the presence of distinct and good diffraction rings at different planes thereby support the presence of polycrystalline structure with narrow particle size distribution which was further supported with the help of XRD studies. EDX measurement shows presence of an atomic ratio in the nanomaterials having a hierarchical architecture with intricate spatial arrangement due to active surface area.



$NiSb_2O4$ $NiSb_2O_4$ $CuAl_2O_4$ $CuAl_2O_4$



$CoFe_2O_4$ $MnFe_2O_4$

FIGURE 6.23

Thermal Gravimetric Analysis and Differential Thermal Analysis

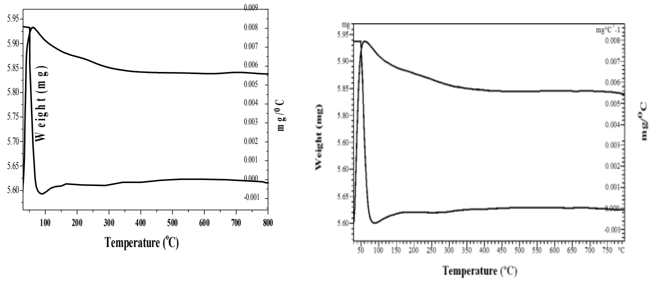
It is a simple analytical technique used to measures the weight loss as a function of temperature. It is also used to measure the materials with their thermal stabilit**y** [104-107]. The analysis was carried out in dry air or in the presence of an inert atmosphere.

Linear relationships exist with different heating rate which can be either being an endothermic or exothermic process. Thermo gram provides data on the chemical and physical transformation .These information helps us to better understand the thermal properties of the materials from ambient temperature to 1000^0C and also help in the determination of purity. TGA/DTA analysis can be performed by using a SDT 2960 Simultaneous Differential Thermal Analyzer (TA Instruments, Inc., New Castle, DE). The instrument was calibrated with gold supplied by Perkin-Elmer. Samples (70 mg) of as-prepared powders were hand pressed in a 3 mm dual action die and placed inside Pt sample cups and then heated at the rates of 10 K/minute from ambient temperature to 1400^oC. The reference material was used as a pellet of α-alumina. A flow of dry air, at the rate of 50 ml/minute was maintained during the experiments.

Differential scanning calorimetric (DSC) is a thermo analytical technique in which the difference in the amount of heat required help to change phase purity with an increase in temperature **.**The sample and reference were heated together and their temperatures were carefully maintained throughout the experiment as a function of time. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters can be measured with the amount of heat absorbed during such transition.

The thermal decomposition of metal alkoxides and its corresponding metal oxide may be described as a smooth stepwise process. The first weight loss occurs below 200^0C and is attributed to be the removal of solvent trapped in molecular system. The second significant weight loss was observed between 250 and 850^0C, which corresponds to the pyrolysis of inorganic residues as indicated by one or more prominent exothermic peak in the DTA curves. No significant weight loss was observed beyond

900^0C in the TGA pattern thus indicating the formation of well-organized crystalline oxides with definite chemical composition. Some of the examples are illustrated in the following figure-6.24.



$NiSb_2O_4$ $CuAl_2O_4$

FIGURE 6.24

Miscellaneous techniques

The following techniques are used for determining the sizes, shapes and structural properties in nanoparticles, bulk and also in a matrix. Electron paramagnetic (spin) resonance (EPR) and nuclear magnetic resonance (NMR) gives information on the electronic structure. Mössbauer spectroscopy, i.e., the resonance absorption of gamma quanta by atomic nuclei in solids is actively used for gaining insight information about an internal structure of an element .The energy of gamma quantum is small (~150 keV), and its absorption excites a nucleus. The resonance condition depends on nucleus excitation energy of a quantum transition, i.e., the difference between the nucleus internal energy in the excited and ground states to takes place. The transition energy in particles depends with the nature of nucleus which gives insight information about microscopic structural properties in a solid material.

NMR studies

The NMR has proved to be very useful technique to achieve a better understanding the hydrolysis and condensation process taking place in bimetallic alkoxide and which help to elucidate their molecular structures at room temperature as well as low temperature. The presence of resonance peaks indicate that the molecules are slightly fluxional and remain mononuclear in solution. The up field chemical shift was observed for nuclei due to their coordination behaviour with metal ion through π bonding.

EXAFS

It is based with the measurements of particle size in the vicinity of the absorption edge, e.g., the K shell. The observed oscillations work as a function of photon energy which results in interference between the primary waves and secondary wave by scattering with the help of neighboring atoms. The analysis of such oscillations allows us to find the distances between adjacent atoms and its deviations with “neighbours” in the particle surface layer as compared to its metal lattices. The information obtained from such deviations helps for better understanding the size, electron density and optic properties in nanomaterial.

X-ray fluorescence spectroscopy

It is based on an excitation of atoms in materials to study the emission in a low-power X-ray tube to produce the secondary fluorescence emission, which falls on the crystal analyzer and then being reflected and registered by a proportional detector. The crystal analyzer and the detector are driven by a goniometer. In doing so, each fixed position of the goniometer corresponds to a definite wavelength to gives rise a secondary emission as selected by an analyzer. The elemental composition was characterized by spectral lines and their intensities are related to the quantitative contents of elements present in a sample. Concentrations are usually computed by comparing the values obtained with the help of standard samples. X-ray fluorescence technique allows us with high-precision analysis of all elements in the Periodic Table in solid, liquid, powder and film samples.

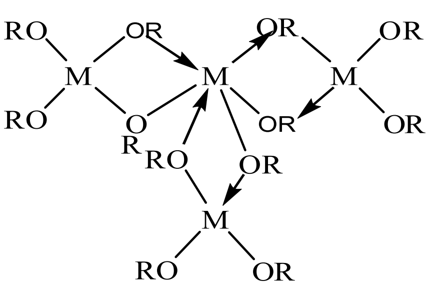
Photoelectron spectroscopy

It is based for measuring the emerging electrons that escape from solids under the action of photons. According to Einstein, the sum of the binding energy of an escaped electron (work function) and its kinetic energy is equal to the energy of the incident photon. From the resulting spectra, the binding energies for electrons and along with their energy levels were studied. These methods allow for studying of an electronic distribution in conduction bands and then analysis with reference to a substance composition with a type of chemical bond used for their interaction between conduction-absorption band electrons within the molecular framework.

Gas absorption Analysis

Inert gas isotherm was taken at -196°C by using ASAP 2010 and 2020 volumetric adsorption analyzer. The sample was degassed under vacuum for at least two hours at 200 °C. With the help of adsorption isotherm specific surface area, pore volume, pore size distribution and other surface related properties can be studied. The adsorption isotherm can be classified as (1). Physical adsorption (physiosorption) governed by Van-der Waals forces between an adsorbed molecule (adsorbat) and a solid surface (adsorbent). (2). Chemisorption takes place due to the formation of surface complexes between active sites on the adsorbent and adsorbate. Physico-sorption is a reversible process and chemisorptions are irreversible [94, 98,106].

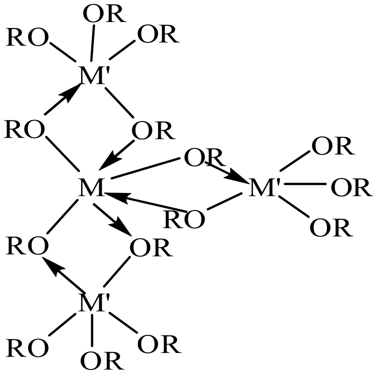
Based on the physico-chemical properties the following structure can be elucidated for bimetallic oxide as follows:



$\left[\{MM'(OR)_4\}_3\right]$

$M = M' = 3^{+}$

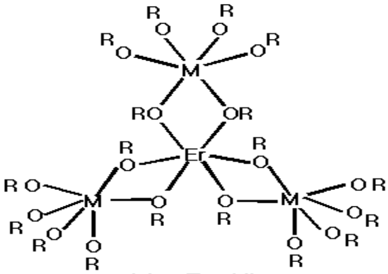
$M = 3^{+}$, $M' = +4$



$\left[M\{M'(OR)_5\}_3\right]$

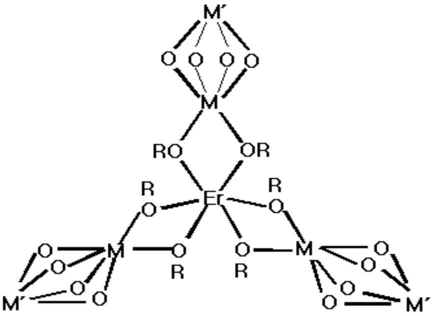
$M' = 4^{+}$, $M = 3^{+}$

Change in molecular structure from molecular precursor to metal oxide



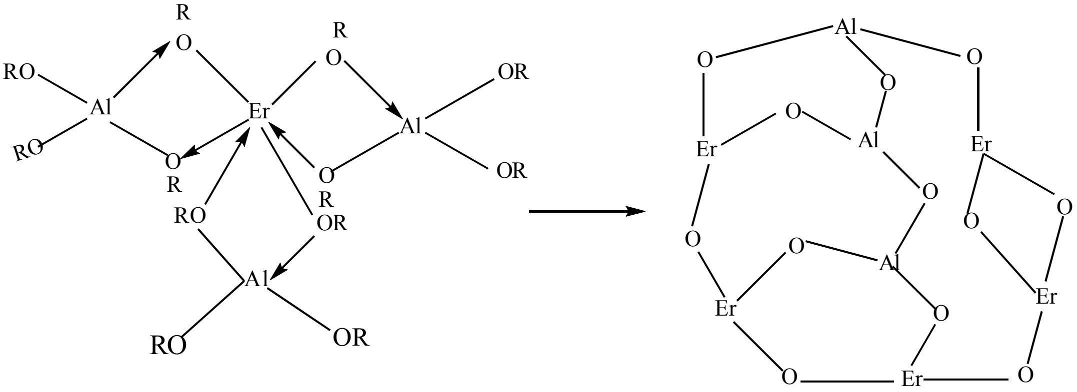
M = Ta, Nb

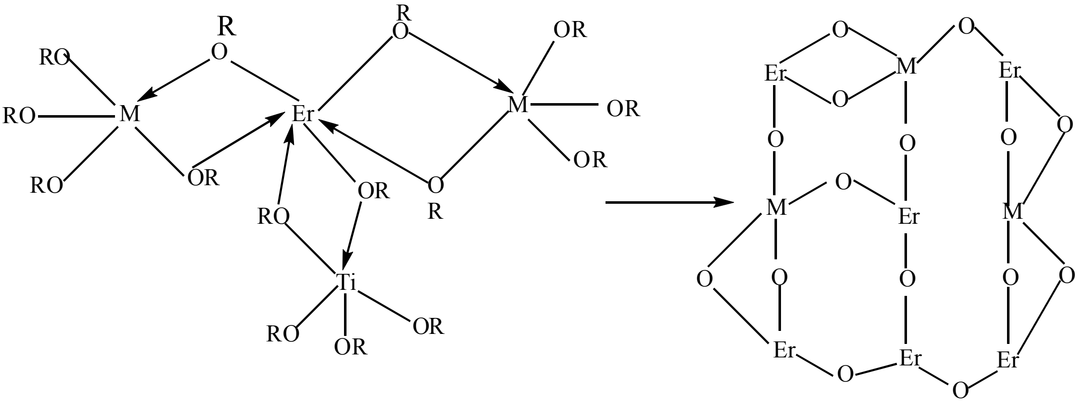
$R = i\text{-}C_3H_7$



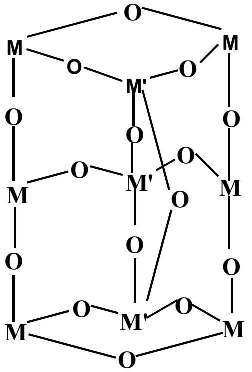
M′= Si, Ti, Zr

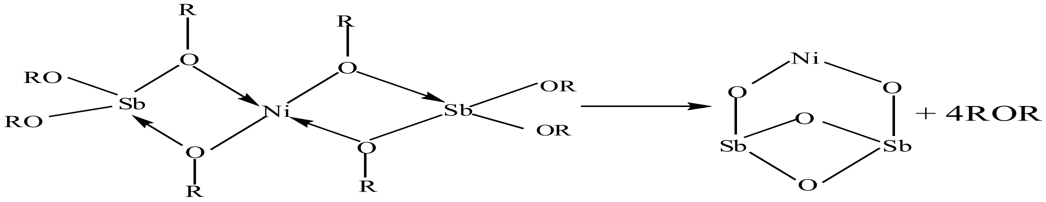
$R = i\text{-}C_3H_7$



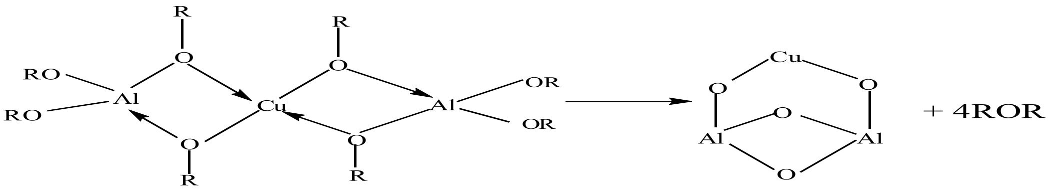


OR

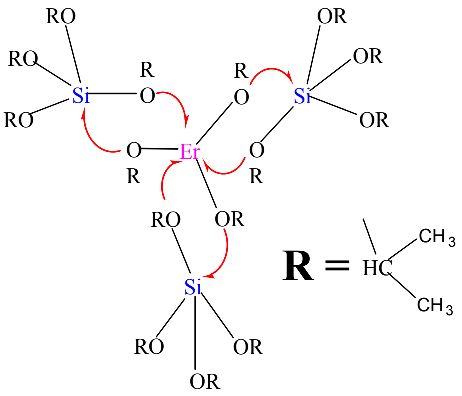


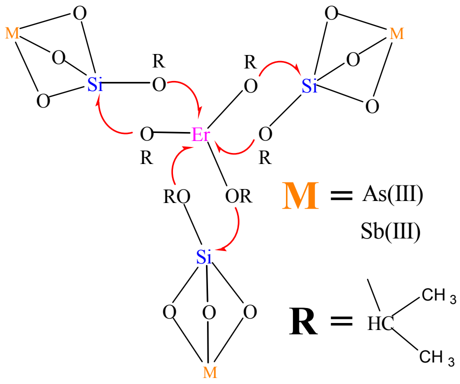


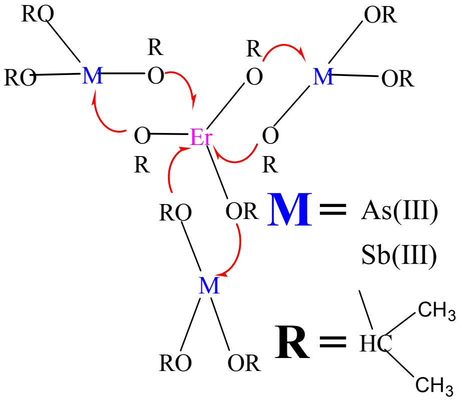
R= $C_3H_7^i$

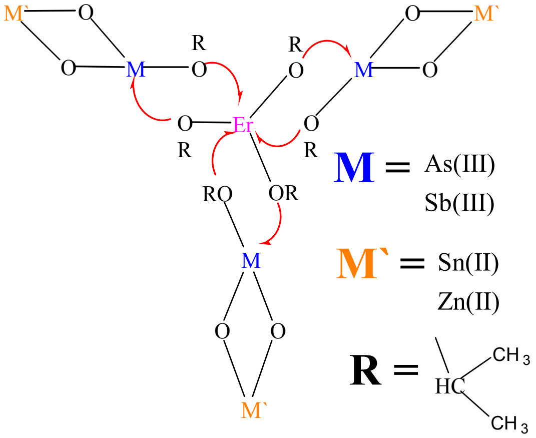


R= C_3H_7









Conclusions

Chemists have an exceptional ability to meet a growing demand from industry by synthesizing a novel cost–effective-eco-friendly molecular precursor and finally design its corresponding nanomaterials by retaining stoichiometric ratio under control by matching physico-chemical and structural properties. The chapter aims on "Molecular recognition" for the synthesis of functional nanomaterial with controlled assembly for its potential use in different technologies via better understanding the process involved at the micro to nanoscale. The synthetic proof-of-concept gives an innovative approach which involves enhancing the surface–volume properties relationship, which depends with the role of metal ion, the purity of the precursor along with its chemical composition. To control uniform active sites with high selectivity-activity-sensitivity remains a synthetic challenge in nanomaterials. The chapter provides a platform for better understanding an interaction of fundamental science and industrial applications with new vistas for improving existing methods for eco-friendly large scale production and cost-effective fabrication of nanodevices.

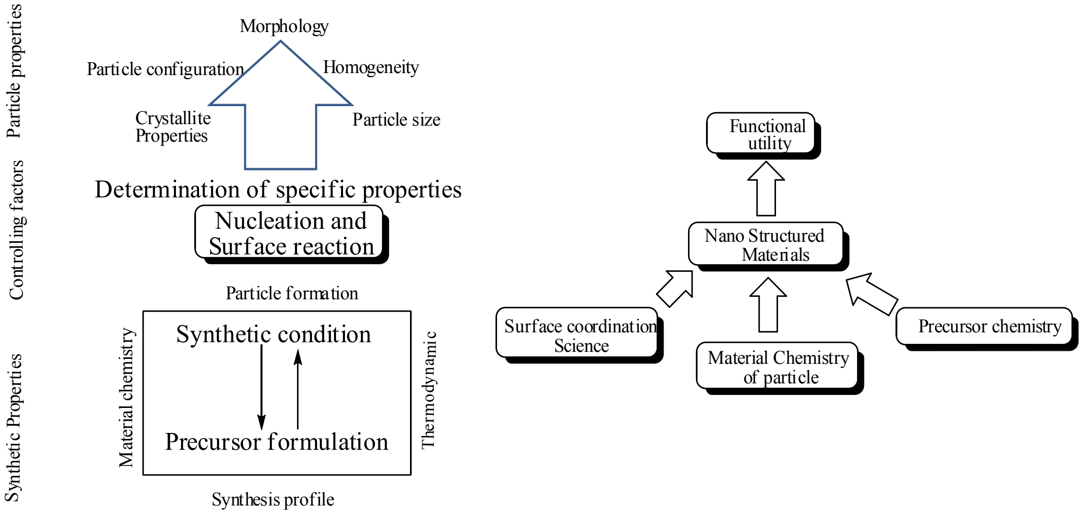


FIGURE 6.25
Properties based applications of nanostructured materials

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