

Synthesis of Oxide Nanomaterials

(Ref: Guozhong Cao; Nanostructures & Nanomaterial: Synthesis, Properties & Applications)

- Oxides particles in colloidal dispersions are generally synthesized by Sol-Gel Processing.
- Core-Shell nanostructures and surface engineering of nanostructures are also synthesized by Sol-Gel Processing.
- The most studied example of Oxide Colloidal is Silica Colloids.

Sol Gel Processing

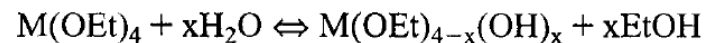
- Sol-Gel processing is a wet chemical route for the synthesis of colloidal dispersions of inorganic and organic-inorganic hybrid materials (Oxides and Oxides based hybrids).
- From such colloidal dispersions, powders, fibers, thin films and monoliths can be easily prepared.
- Offers many advantages, like low processing temperature and molecular level homogeneity.
- Useful in making complex metal oxides, temperature sensitive organic-inorganic hybrid materials, thermodynamically unfavourable or metastable materials.

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Typical Sol-Gel processing consists of HYDROLYSIS and CONDENSATION of precursors.

- **PRECURSORS:** Metal Alkoxides, Organic/Inorganic salts.
- **SOLVENTS:** Organic or Aqueous solvents.
- **CATALYSTS:** Often added to promote Hydrolysis and Condensation reactions.

Hydrolysis:



Condensation:



- Hydrolysis and Condensation reactions are multiple step processes, occurring sequentially and in parallel to each other.
- Each sequential reaction may be reversible.
- Condensation results in the formation of nanoscale clusters of metal oxides or hydroxides along with organic groups embedded/ attached to them.
- Organic groups exist due to either incomplete hydrolysis or introduced as non-hydrolysable organic ligands.
- Size of nanoscale clusters, along with morphology and microstructure of the final product can be tailored by controlling the hydrolysis and condensation reactions.
- To synthesize colloidal dispersions of multiple components, challenges are to ensure hetero-condensation reactions between different precursors having different chemical reactivities.
- Reactivity of metal atom depends on the extent of charge transfer and ability to increase its coordination number.

- As a rule of thumb, electronegativity of metal atom decreases and ability to increase its coordination number increases with their ionic radius.

Electronegativity (χ), partial charge (δM), ionic radius (r) and coordination number (n) of some tetravalent metals

<i>Alkoxide</i>	χ	δM	$r(\text{\AA})$	n
Si(OPr ⁱ) ₄	1.74	+0.32	0.40	4
Ti(OPr ⁱ) ₄	1.32	+0.60	0.64	6
Zr(OPr ⁱ) ₄	1.29	+0.64	0.87	7
Ce(OPr ⁱ) ₄	1.17	+0.75	1.02	8

where OPrⁱ is OCH₂CH₂CH₃

- Chemical reactivity of alkoxides increases with ionic radius.
- Several ways exist to ensure hetero-condensation and to achieve a homogeneous mixture of multiple components at the molecular/atomic level.
- Precursors can be modified by attaching different organic ligands.
- For given metal atom/ion, large organic ligand or more complex organic ligand would result in less reactive precursor.

Example:

$\text{Si}(\text{OC}_2\text{H}_5)_4$ is less reactive than $\text{Si}(\text{OCH}_3)_4$

- Another way to control the reactivity of the alkoxides is to chemically modify the coordination state of the alkoxides with chelating agent such as acetylacetone.
- Multiple step sol-gel processing is another way to overcome this problem.
- Less reactive precursor is first partially hydrolysed and more reactive precursor is hydrolysed later.
- In more extreme cases, one precursor can be fully hydrolysed first and all water is depleted.
- If hydrolysed precursor has very low condensation rate, then second precursor is introduced and forced to condensate with the hydrolysed precursor by reaction:



- Condensation reactions are only limited between hydrolysed less reactive precursor with more reactive precursor



- Incorporating organic components into an oxide system by sol-gel process makes it easy to form organic-inorganic hybrids.
- One approach is to co-polymerize or co-condense both the inorganic precursors, which lead to the formation of the inorganic component, and organic precursors consisting of non-hydrolysable organic groups.
- Such organic-inorganic hybrids are a single-phase material, wherein organic and inorganic components are linked through chemical bonds.
- Another approach is to trap the desired organic components physically inside the inorganic or oxide network by either homogeneously dispersing the organic components in the sol, or infiltrating the organic molecules into the gel network.
- Similar approaches can be applied for the incorporation of bio-components into oxide systems.

- Constituent precursors may exert a catalytic effect on one another leads to a big challenge in making complex oxide sols.
- It results in different reaction rates for hydrolysis and condensation processes when they are mixed together as compared to the precursors processed separately.
- In the sol preparation, much attention has not been given to control the crystallization or formation of crystal structure.
- Formation of crystalline structure of complex oxides without high temperature firing is desired for some applications.
- Matsuda and co-workers have demonstrated the formation of crystalline phase of BaTiO_3 without high temperature sintering by controlling processing conditions including concentrations and temperature.
- In spite of several synthesis approach, there is still a lack of general understanding on the control of crystallization of complex oxides during sol preparation.

- By a careful control of sol preparation and processing, monodispersed nanoparticles of various oxides, including complex oxides, organic-inorganic hybrids and biomaterials can be synthesized.
- The key issue is to promote temporal nucleation followed by diffusion-controlled subsequent growth.
- The particle size can be varied by changing the concentration and aging time.
- Nanoclusters formed by hydrolysis and condensation reactions have a size ranging from 1 to 100 nm.
- In the formation of monodispersed oxide nanoparticles, the stabilization of colloids is achieved by electrostatic double layer mechanism.
- This is the reason that polymer steric diffusion barrier existing in the formation of metal and non-oxide semiconductor colloids is not present in the formation of metal oxides.
- Diffusion controlled growth in such a cases is achieved by other mechanisms, such as controlled release and low concentration of growth species in the sol.

Forced Hydrolysis

- The simplest method for generation of uniformly sized colloidal metal oxides is based on forced hydrolysis of metal salt solutions.
- By increasing temperature, most of the polyvalent cations readily hydrolyze and deprotonation of coordinated water molecules is greatly accelerated.
- In general, hydrolysis products are intermediates to precipitation of metal oxides and hence increasing temperature results in an increasing amount of deprotonated molecules.
- When concentration exceeds the solubility, nucleation of metal oxides occurs.
- To produce metal oxide colloids, one just needs to age hydrolysed metal solutions at elevated temperature.
- In general, hydrolysis reaction should proceed rapidly and produce an abrupt supersaturation to ensure a burst of nucleation, resulting in formation of large number of small nuclei, leading to formation of small particles.

- This principle was demonstrated by Stober and co-workers in the formation of silica spheres.
- The procedures for the preparation of silica spheres were simple and straight forward.

Precursors: Various silicon alkoxides with different alkyl ligand sizes

Solvents: Various alcohols

Catalyst: Ammonia

- Initially, alcohol solvent, ammonia and a desired amount of water were mixed and then silicon alkoxide precursor was added under vigorous stirring.
- Formation of colloids or the change in the optical appearance of the solution became noticeable just in a few minutes after the addition of precursors.
- Depending on the precursors, solvents and the amounts of water and ammonia used, spherical silica particles with mean sizes ranging from 50 nm to 2 μm were obtained.

Synthesis of iron oxide nanoparticles (Forced Hydrolysis)

- Preparation of spherical colloidal α -Fe₂O₃ nanoparticles of 100 nm size is another example of forced hydrolysis.
- FeCl₃ solution is mixed with HCl and diluted.
- Mixture is then added into preheated H₂O at 95-99°C with constant stirring.
- Solution is kept in a sealed preheated bottle at 100°C for 24 hr before being quenched in cold water.
- High temperature favours a fast hydrolysis reaction and results in high supersaturation, leading to the formation of a large number of small nuclei.
- Dilution before heating to high temperatures is very important to ensure a controlled nucleation and subsequent diffusion limited growth.
- Long aging period would permit the occurrence of Ostwald ripening to further narrow the size distribution.

Controlled release of ions

Controlled release of anions/cations has a significant influence on the kinetics of nucleation and subsequent growth of oxide nanoparticles and is achieved by spontaneous release of anions from organic molecules.

- It is well known that solutions of urea, $\text{CO}(\text{NH}_2)_2$, when heated liberate hydroxide ions, which can cause precipitation of metal oxide/hydroxide.
- Decomposition of urea is used to control the nucleation process in the synthesis of Y_2O_3 : Eu nanoparticles.
- Yttrium and europium chlorides were dissolved in water and the pH was adjusted to ~ 1 with HCl or KOH.
- An excess of urea, typically 15x, was dissolved into the solution.
- The solution was then raised to $> 80^\circ\text{C}$ for 2 hours.
- The urea decomposed slowly and there was burst of nucleation when a certain pH value of $\sim 4-5$ was reached.
- In general, certain types of anions are commonly introduced into the system as catalyst.

- In addition to the catalytic effect, anions commonly exert other influences on the processing and the morphology of the nanoparticles.

A brief summary of synthesis parameters including temperature and time of aging are used to obtain α -Fe₂O₃ (A, B, and C) or β -FeO(OH) nanoparticles.

	Fe^{3+} (M)	Cl^- (M)	<i>Initial pH</i>	<i>Final pH</i>	<i>Temp</i> (°C)	<i>Time</i>
A	0.018	0.104	1.3	1.1	100	24 hr
B	0.315	0.995	2.0	1.0	100	9 days
C	0.09	0.28	1.65	0.88	100	24 hr
D	0.09	0.28	1.65	0.70	100	6 hr

Synthesis of zinc oxide (ZnO) nanoparticles (Controlled release of ions)

- Preparation of crystalline ZnO nanoparticles is another example of controlled release of anions.
- Initially, zinc acetate is dissolved into methanol to form zinc alkoxide precursor solution.
- Then zinc alkoxide precursor is hydrolysed and condensed to form zinc oxide colloid with lithium hydroxide as a catalyst with sonication at 0°C or room temperature.
- Sonication accelerates the release of OH^- groups, resulting in immediate reaction to form a stable ZnO sol.
- Use of NaOH, KOH or $\text{Mg}(\text{OH})_2$ all produces turbid precipitates.
- ZnO nanoparticles are ~3.5 nm in diameter in fresh sols and ~5.5 nm in 5 day old ones.
- Aging of alcoholic ZnO colloids is known to produce larger particles.
- Acetate groups are believed to attach to the surface of ZnO colloids and thus stabilize the colloidal dispersion.

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