

STABILIZATION OF NANO-PARTICLES IN STAINED GLASSES

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1 Introduction

Imagine standing in a medieval church, as eyes adjust to darkness, you notice colored light streaming down from stained glass windows. The churches use the stained glass to tell the stories and morals of the Bible. Noble metals are most usual particles in stained glass. Colors or stains appear when heated glass is doped with colloidal solutions of metals and annealed.

People had lot of interest in optical properties of noble metals especially gold from the times of Romans. They tried many forms of gold and silver to get varied colors. Lycurgus Cup(fig) is one such an artifact[1]. It is dichroic which uses gold and silver nano particles. This way ancient glass makers utilized nano particles. They were able to control the size of metal nano particles using some chemicals without knowing how they got those colors moreover it was considered as an art. A famous colorant in glass 'Purple of Cassius'(fig 2) is a colloid resulting from the hetero-coagulation of gold particles and tin oxide.[2]



Figure 1: Lycurgus Cup in reflected and transmitted light respectively



Figure 2: 'Purple of Cassius' Chinese pottery

The colors may arise from scattering of light by colloidal metals in glass plus pigmentation from metallic oxides. The colors produced depends upon the precise colloidal concentration and the particle diameter and are highly dependent on the proportions and oxidation states of certain elements, the time and temperature of heating and probably the atmosphere during heating. After all, stabilization of those nano particles from coarsening is the main task in order to get expected color. One has to take care of Oswald Ripening and nucleated grains radius should not exceed critical radius. The most common use of making colloids is use of polymer stabilizers and ionic liquids[3].

2 Nucleation control

To suppress the Ostwald ripening, the nuclei should be as small and mono-sized as possible. This will happen if nucleation of all nuclei occur at ap-

proximately same time and same conditions. In practice, to achieve a sharp nucleation, the concentration of the growth species is increased abruptly to a very high supersaturation and then is quickly brought below the minimum concentration for nucleation. Also increase in supersaturation increases volume gibbs free energy which in turn decreases critical radius serving our purpose.

$$\Delta G_v \equiv (4/3)\pi r^3 + 4\pi r^2 \gamma$$

$$r^* \equiv -2\gamma/\Delta G_v$$

$$\Delta G^* = 16\pi\gamma/3(\Delta G_v)$$

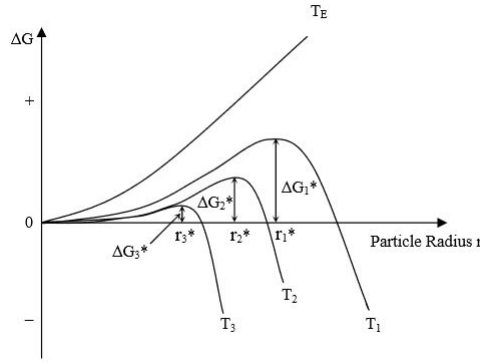


Figure 3: critical radius and critical volume gibbs free energy for diiferent supersaturations

Rate of nucleation is directly proportional to concentration of solute and thermodynamic fluctuations of gibbs free energy.

$$R_v \propto C_o e^{(-\Delta G^*/KT)}$$

This equation indicates that high initial concentration or supersaturation (so a large number of nucleation sites), low viscosity, and low critical energy barrier are favors the formation of a large number of nuclei. For a given concentration of solute, a larger number of nuclei mean smaller sized nuclei.

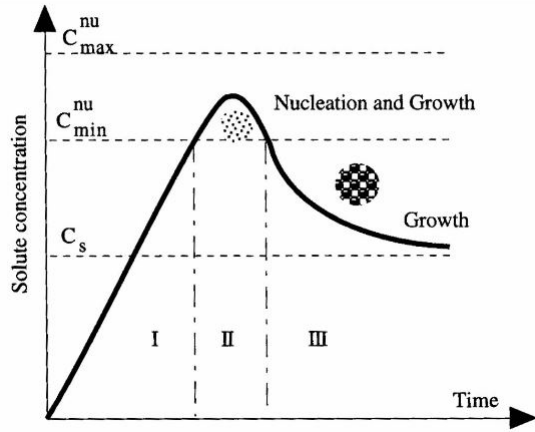
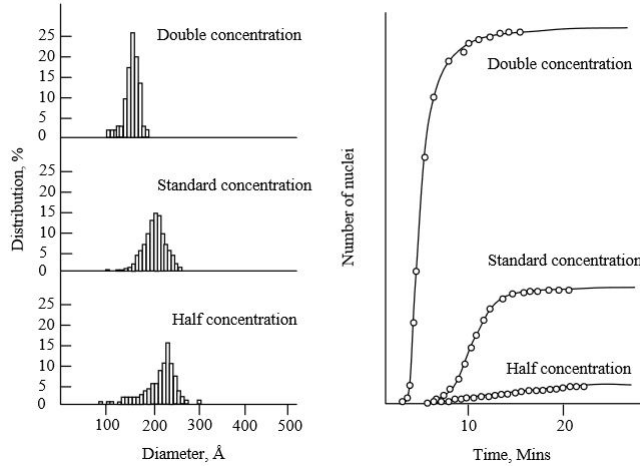


Figure 4: Nucleation and growth seen with variation in solute concentration and time

Below this min concentration, no more new nucleus forms, whereas the existing nuclei continue to grow until the concentration of the growth species reduces to the equilibrium concentration. The size distribution of nanoparticles can be further altered in the following growth process. And while preparing metal colloids of nano scale, very strong reducing agents are used to make reaction fast and obtain high concentrations. In below figure distribution of particles over range of radii is very low at higher concentrations.

3 Grain growth control

Grain growth requires generation of growth species, diffusion of the growth species from bulk to the growth surface, adsorption of the growth species onto the growth surface and surface growth onto the solid surface. Nanoparticles have a particular tendency to lower their very high surface energy, due to high surface to volume ratio. Bare nano particles tend to stabilize themselves either by sorption of molecules from the surroundings or by lowering the surface area through coagulation and agglomeration. Ionic liquids provide stability to nano particles from diffusion using electrostatic and steric forces.

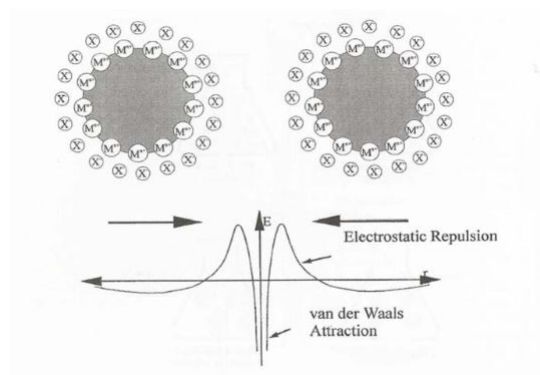


1.JPG

Figure 5: (left)particle size distribution of gold sol prepared at different concentrations and (right) Nucleation rate of gold sol prepared at different concentrations

3.0.1 Electrostatic stabilization

When an ion approaches a non grounded non charged nano particle, then it induces charges on it and forms a dipole. But net charge on the metallic sphere becomes zero. The total electrostatic potential energy is sum of potential of external charge and induced dipole. But latter is more making total potential energy positive. So, the charge is attracted towards to the metal particle. And with increase in number of approaching charges, energy becomes small.If cations and anions approach the metal particle then it is predominantly surrounded by one type and other type forms a shell. This formation of double layer makes two metal particles repulsive.The mechanism is according to DLVO theory.



3.JPG

Figure 6: Electrostatic stabilisation of metal colloids. van der waals attraction and electrostatic forces compete with each other

3.0.2 Steric stabilization

Steric stabilization is based on the steric repulsion between molecules or ions adsorbed on neighboring particles. Size and chemical nature of these molecules determine the degree of stabilization. Due to geometric constraints around nanoparticles bulky molecules gives stabilization and an elongated or conical geometry is advantageous to keep the approaching nanoparticles apart. When the length of the stabilizer is significantly longer than the characteristic size of the nanoparticles, a sphere can be formed encapsulating the nanoparticle. Because of that, high molecular weight polymers are often employed as stabilizers for nanoparticles. And also has to be adsorbed strongly enough on the surface of the nanoparticles to provide long residence time. When a stabilizer provides more than one adsorption centre, the chelating effect can increase the probability that the stabilizer remains adsorbed. Thus multi valent molecules are used as adsorbents.

The polymeric stabilizer is also known as a capping material. The monolayer of the polymer affects the growth process significantly. If the growth sites are occupied by the polymer, the rate of growth of nanoparticles may be reduced. If the polymeric stabilizer completely covers the surface of the growing particle, it may hinder the diffusion of the growth species from the surrounding solution to the surface of the particle. The shape and size of the nanoparticles[4] can be varied by the use of different amounts of different polymeric stabilizers.

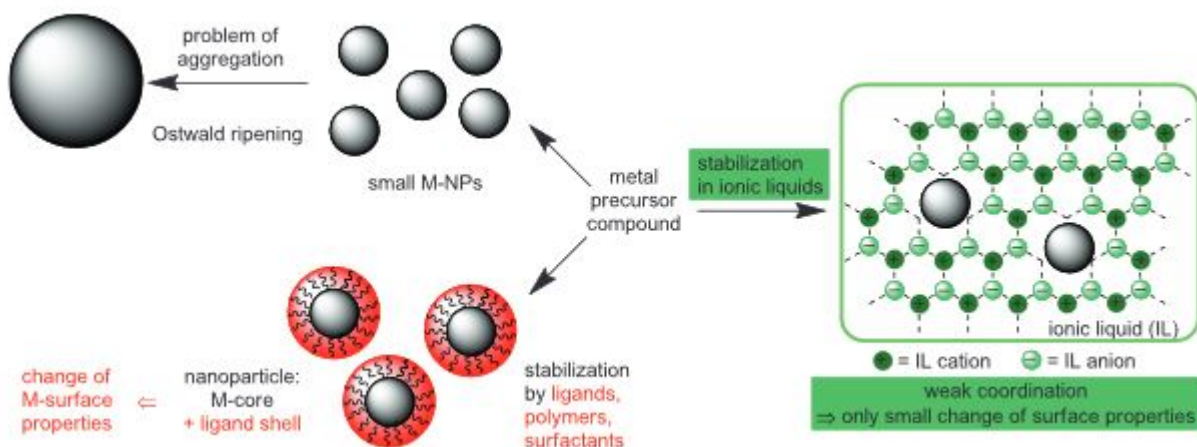


Figure 7: Overall map of stabilization with ionic liquids

During formation of nano particles, polymers can bind to specific surface giving desired shape and aspect ratio. Due to the high ion density, ionic liquids enable particularly strong electrostatic stabilization, while at the same time they can be selected in such a way that either the cations or the anions are strongly chemisorbed, and either the cations or the anions have the appropriate bulky geometry.

4 Certain examples of praperation of size controlled metal colloids

1. gold nanoparticles (Au NPs, 2-6 nm) capped with glutathione by varying the pH (between 5.5 and 8.0) of the solution before reduction. Less pH produced large precursors which in turn led to formation of large gold nano particles.[5]

2. Turkevich Method of preparation: Gold chloride is dissolved in water while heating and stirring. TriSodium Citrate dihydrate is dissolved in a small amount of water and then added to gold chloride solution. Refluxed for one hour forming gold nano particles. Gold nano particles size is said to be dependent on citrate concentration.[6]

3. Brust Method: Chlorauric acid solution with tetraoctylammonium bromide (TOAB) solution in toluene and sodium borohydride as an anti-coagulant and

a reducing agent.[7]

4. Michael Faraday prepared pure colloidal gold using phosphorus to reduce gold chloride. He was the first to find out gold colloids are giving ruby color.[8]

5. Even physical methods are used selectively in formation of nano particles.[9]

5 Conclusion

The stained glasses have been produced in almost same way from hundreds of years. It include formation of metal colloidal solutions of nano size in order to get different colors using optical properties of metals by varying their size. In the most commonly practiced methods of preparation of colors to stained glass one need a precursor , a reducing agent and a polymeric stabilizer. When the synthesis process is not controlled the particles gets coarsened by oswald ripening which results in different color than expected. With further increase in size of grains results loss of color.

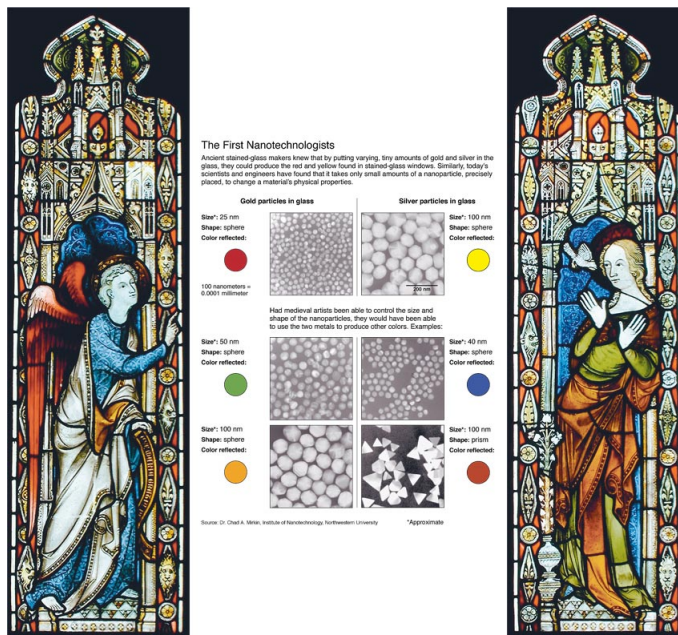


Figure 8: Variation in color with variation in size of gold and silver nanoparticles

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