



Advancement Of Monometallic Nanoparticles To Bimetallic Nanoparticles And Their Composites

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Abstract

Metal nanoparticle in ionic liquid media has various impacts in many fields which include research areas, technology, energy, and many other fields of science. Since we know that when we use two different metal combinations during synthesis, we obtain bimetallic nanoparticles (BMNPs). In recent years BMNPs have been concerned with great consideration as compared to Monometallic NPs in many fields like medical, technology, or systematical science because bimetallic NPs show unlimited properties. In our presentation, we will discuss the synthesis of bimetallic NPs including Cu or Cu₂O or Fe and their oxide or Ag-Cu, Fe-Cu nanoparticles combination. Bimetallic type's nanoparticles show greater surface reactivity, thus being used to improve interfacial and catalytic activities.[1-2] for example- Ag is mixed with Cu to create Ag-Cu alloy NPs, which can be used to improve the oxidizing property of Cu NPs. Various methods are described in the literature for its synthesis but our presentation mainly covers the chemical reduction methods for NPs synthesis. It will also be explained that BMNPs nanocomposites have better quality as compared to bimetallic nanoparticles. A huge application zone of bimetallic nanocomposites involved industries, medical drug delivery, aqua field sanitization, and chemical industries as many more.

Reference

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A.D. Verma, S. Pal, P. Verma, V. Srivastava, R.K. Mandal, I. Sinha, J. Environ. Chem. Eng. 5 (6) (2017) 6148.

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1. Introduction

1.1 Nanotechnology

In nanotechnology, The preface nano is taken from Grecian word “nanos” which sense “dwarf” this means to things of one billionth in size. the elementary idea of nanotechnology was state in the average of 20th period by Richard Feynman, he is an American physicist, the world is known as the “Father of nanotechnology” and he elucidated in American physical society meeting which is detained in 1959, that how ecosphere’s all files can fitting in a booklet. At that moment, his speech transported a great rebellion in the ground of science & technology. He also described various procedures we used by this procedure to convert the specific particles or fragments from one form to other lesser form by using many sets of apparatuses. Nanotech expression was created by Norio Taniguchi which was Tokyo University of Science. That was Abundant mindfulness was awakened between the people nearby nanotechnology when the manuscript inscribed by Eric Drexler named “Engines of creation” was printed. He explained in that book about nanotechnology and its many term.

similarly many more scientists have used the above-mentioned methods expansively for the research of bimetallic elements, but when we study some over the ancient era then we see many more bimettalic and their oxide NPs for ex. Zn & zno Ag-Cuo₂, Au-Pt, Co-Ni, Ag-Pd, and fe₂ ,Fe-Pt and unfluctuating the elements like Cu, Pb, Au, Ni, Co, Pt, Fe and ag. Significantly we concern were directing on the multiused reducing agent, which act as solvent, reagent, stabilizer, and as well as, which inhibites the elements development and avoid accumulation. normally, in the research method of bimetallic particles by wet chemical method, each elements in this reaction medium nucleate and then produce separately due to the variation of the reduction abilities. Which leads to the growth of hetero-structured substitution. And also helps in our life cycle like dipping the use of manufacturing substances and creation of good the environment, healthy, safe and wealth living. In addition to this, it can be used for water handling, cancer treatment and food packaging and many more etc.

1.2 Nanoparticles

Nanomaterials or Nanoparticles (NPs) are the micromillimeter- sized solid subdivisions or particles caused at nuclear or molecular scale so to formulated either new or greater physical possessions which is not possible by conservative substance solids. These nanosize particles or nanomaterials act as a comprehensive unit in relative properties. as we know All constituents have few serious variety or value under which their quality fluctuations extremely. Molecules or Particles under 100 nm in distance express properties that are dissimilar from those of conservative solids. We also understood that When all the magnitudes of the particle are in nm range, then it is called iso dimensional NPs, for example round shaped nanoparticles of silica or silicon oxide. And The description of nanoparticles may fluctuate for different area and changed materials. for hypothetical point of view, “nanoparticles are frequently called Nano clusters or simply clusters which are defined as the combination of millions of atoms or molecules ;(Ferrando et al., 2008). atoms or particles may be similar or of different type. Nps can be of formless or crystal-like form and their sides or surface can act as a carrier for liquid condensations or vapour or gases.

Medicine or the drugs can dissolve, entrap, capture or attach to a nanoparticle environment. Nanoparticles should be summerised as a separate state of matter for instance crystal shaped NPs form (carbon form and fullerenes nanotubes) and old or traditional crystalline solid forms (diamond and graphite). Several writers bounded the extent of nano particles among 10-100 nm.

The nanoparticles can be produced by these two techniques firstly ; top- down approach and bottom- up approach. And In top- down method, the unpackaged or substance materials are fragmented or broken down to the NPs; though, in bottom- up method, the nanoparticles associated and to form the bulk material.

synthesis of Ag and Cu nanoparticles can be categorized into top-down and bottom-up approaches. These two approaches can be subcategorized into variety synthesis techniques and this article is no intention to cover in detail of all techniques as several articles have been widely covered (Biswas et al. 2012; Parak et al. 2010). In brief, top-down approach refers to use bulk Ag or Cu mechanically reduces its size into nanoscale (Gates et al. 2005; Niemeyer 2001). Conversely, bottom-up approach refers to build up of Ag or Cu nanoparticles by self assembly of atoms or molecules (Zhang 2003; Liz-Marza ´n and Kamat 2003).

The top down method is simple but The bottom- up approach is more appropriate or suitable because in this, the

chances of adulteration are quite high. The nanoparticles are of excessive position in our daily life. For example, nanoparticles of TiO_2 are one of the utmost important elements of suntan lotion products. because Its only visible light to pass over the skin while scatter the damaging uv rays. Nanoparticles is the basis of nanotech. And all These method and technics are used in different forms dependent upon the kind of application or use.

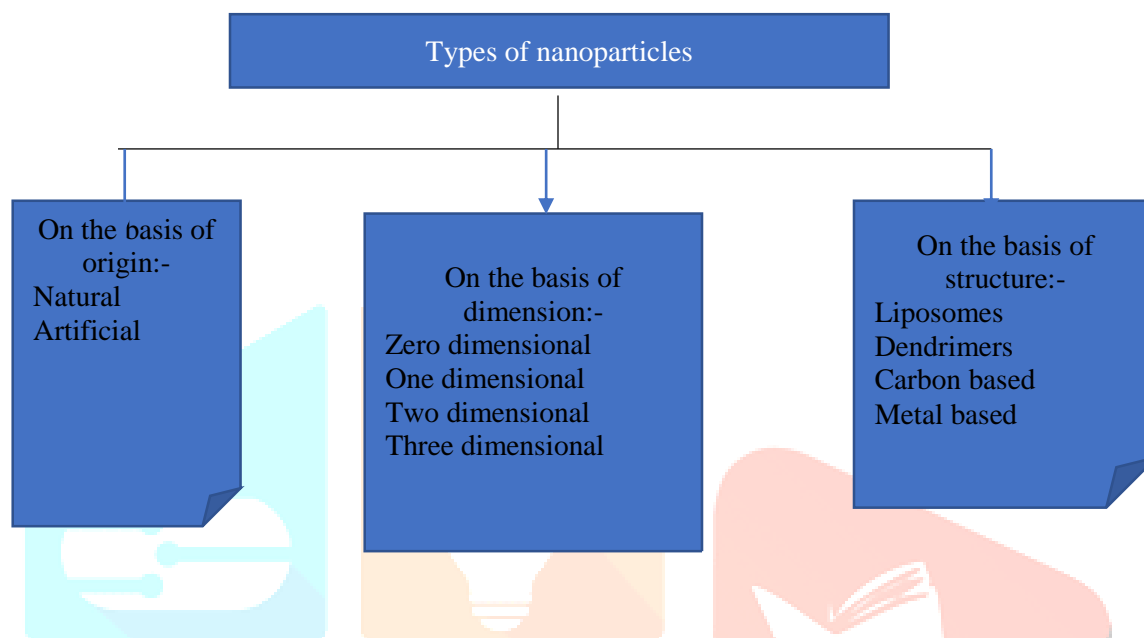


Fig1: flowchart of nanoparticle's types

Monophonic or Monometallic nanoparticles :-

The monophones or Monometallic nanoparticles (MNPs), as the name proposes, contain of only one or single metal like Ti, Cr, V etc. The established metal atom determines the possessions of these nanoparticles. The monometallic NPs are of different kinds dependent upon the type of metal or element or molecules existing such as magnet type, metallistic and conversion or transion metal nanoparticles, etc. Those can be arranged by different ways but vary suitable & most significant method is called the chemical or chemical reduction method. Their specific structure can be alleviated by using several useful functional groups. In past recent few times have obvious the larger attention in mono or bi-metallic nanoparticles field because their physical and chemical properties vary improved and usefull. Therefore, they are used in a numerous field in our daily life products and its related industries for example in dairy field, in electronic, in drinking area treatment, in cosmetic and catalyst reagent etc.

moreover, they have also been used as antibacterial or antiviral, antimicrobial agents which they inhibits many type of microorganisms for instance Solmonela or vibrio colera, *Escherichia coli* (Sondi and Salopek-Sondi, 2004), *Streptococcus pyogens* (Nanda and Saravanan, 2009) and *Bacillus subtilis*(Rai et al., 2009). *Streptococcus mutans* (Espinosa- Cristóbal et al., 2009).

Di or Bimetallic nanoparticles(BMNPs)

Basically, BMNPs collected two different-different metal which combine to form a greater awareness than the monometallic nanoparticles from both scientific as well as technological point of view (Sharma et al., 2016b; Toshima and Yonieawa, 1998). Founding metals and their nanometric extent determine the properties of the bimetallic nanoparticles. These are synthesized by the combination of different manners of metallic nanoparticles. the propensity of enhancing the energy of Plasmon absorption band of metallic mixture, these are actually suggest or offers us a multiuse means for biosensing. All these properties may contrast from those of pure elemental

materials and comprise unique size dependent thermal, catalytic, optical and electronic, properties. a wide-range research in the field of bimetallic nanoparticles in progress just a period back. Several preparation methods have been proposed for their preparation and complete classification. Now, this time investigators are focusing on selected formulating new bimetallic nanoparticles in different different forms, such that composites or alloy form, core-shell, and contact aggregation form. Essentially, complete bimetalization, the catalytic properties of the resulting nanoparticles can be expanded to great extent which is not be realizable by the use of monometallic catalyst. The electronic effect plays an important role in bimetallic catalyst, which defines the charge transfer. Composites or alloy of the establishing elements can result in the structural changes of the bimetallic nanoparticles. "From monometallic to bimetallic nanoparticles, an extra degree of freedom is introduced (Sharma et al., 2015)" The activities of catalyst of different bimetallic nanoparticles have been then compared. After that with the help of some physical and spectroscopic dimensions we can develop some new methods and correlations. These preparation methods and conditions determine the structure and miscibility of the two metals in bimetallic nanoparticle. Generally, bimetallic nanoparticles are prepared by instantaneous reduction of two metal ions or particles in the existence of appropriate equilibrium approach for example steric hindrance & static-electronic repulsive energy. When we use this type method then a particle structure between core shell and homogeneous or similar compound depending on the reduction condition is gained. we can have control over the reduction rates of the two mechanisms by supervisory the size, shape and NPs structure.

1 Methods of synthesis of nanoparticles

Since then time to time many scientists or researcher have discovered many more new methods but some methods are vary effective & appropriate to prepare nanoparticles which are of the essential magnitude, alignment, size and shape because these features greatly effect the properties of the compound. here we discuss about Some of the preparation methods which is used for the synthesis of the nanoparticles(NPs) are:-

2.1 Photochemical and Thermal decomposition method:-

When we discuss about thermal method this is endothermic in nature due to high energy condition for the bond breakage. It includes the pyrolysis of precursors in boiling solvents at high temperature but the main difficulty of this process is that under such high temperature, the separation of unstable nanocrystal phase from the reactive phase becomes very difficult. generally thermal method is endothermic in nature. Photochemical method simplifies the isolation and its occurs in the presence of light and organic compounds by exposing the surface to UV light through a photomask for ex: calcium carbonate breaking into calcium oxide and carbon dioxide and many other decomposition.

2.2 Electrochemical Reduction

Electrochemical method is vary simple and we make ions electrode for use, in this process electricity is used as the controlling or regulatory force. "The electric current is passed between the two electrodes which are separated by electrolyte" (Katwal et al., 2015). Investigators used electrochemical method for the preparation of metallic nanoparticles such as NaCl, BaCl, AgCl etc. This dissolved the metallic anodal sheet and metallic salt formed. it was reduced by the cathode to metallic particles. These ionic elements formed were stabilized by tetraalkylammonium salines. Advantages of electrochemical technique consist of low cost, high purity of particles, constituent part size control by adjusting the current concentration & density and over view this is simple process of operation. When we see the progress of industries then confidently we said that this method is mainly used in industrial field. Like dyes industries, chemical industries, alkaline earth metal and alkali metals like Na, Li etc obtained by electrodeposition from molten salts, cosmetic field many more industrial use.

2.3 Sputtering:-

Furthermore, sputtering is to use the energy of partially ionized gas on the surface. Discharge of nanoparticles takes place only when the spread of energy providing is high as equated to the conservative thermal energies. and this method produces nanoparticles of high purity. For example, silicon are prepared using magnetic sputtering method.

This process agonizes disadvantages such as fewer control over the geomorphology of particle and energy consumption for the exclusion of electron is vary high. Subsequently high temperature is essential; it can be damaging skin and create various skin diseases.

2.4 Sol-gel method:-

The above sound “sol-gel” taken from two words i.e. sol and gel. The sol is a constant suspension of colloidal compact particle in liquid. And The dispersed phase in sol is small that there only Vander- Waal forces. Then In gel, the concentration of solid is more than fluid or liquid. It is a semi- rigid form wherein the particles or ions left after the vanishing starts to form a network. Whereas the gel systems, there are the covalent interactions. The mixture of these two systematic functions is called sol-gel method. These are consists of two reactions, which is hydrolysis and condensation. Numerous BMNPs are synthesized by this method such as Ag-au, pd-Ag and Pt-Au etc. This is vary useful because it is a less financial and effective method to produce good quality nanoparticles (Sharma et al., 2016). So It is quite interesting subsequently it is a low temperature procedure.

2.5 Chemical Precipitation method: -

it is the procedure of reformation of a solution into solid by varying the matter into insoluble form.” This situation involves the adding of chemical components and then separation of precipitation from the solution” (Sharma et al., 2016b). clean particles of ZnO and ZnS can be ready by this method. Afterward it is a single phase and supports in big scale invention of nanoparticles in unpolluted form.

2.6 Micro-emulsion method

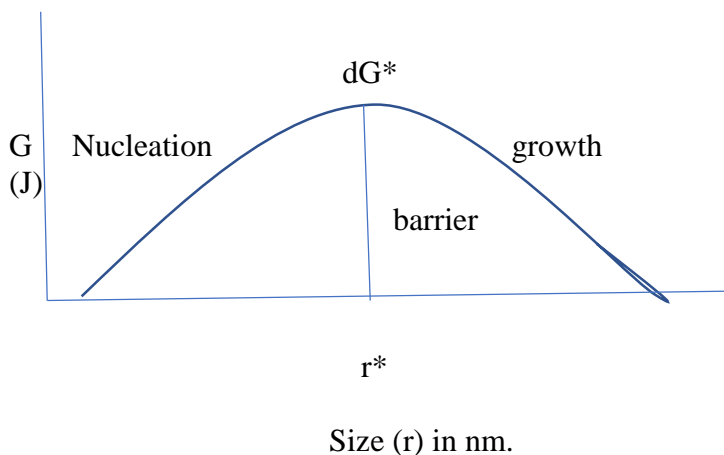
We can define this as a solution which is composed of as a minimum three components these are a polar , a non-polar component and a surfactant. The purpose of the surfactant is to form a layer between the polar and non- polar component. Although it is thermodynamically constant and similar in nature. Which may be classified into two catagery; water-in-oil (w/o) or oil-in- water (o/w), dependent upon the category of spread and continuous segment. a few organic nanoparticles can be equipped using oil in water micro-emulsion. Pd-Au bimetallic nanoparticles which stand supported on nickel foil substrate via in-situ self-assembly of irreversible micro emulsion of water/Triton X-100/n-hexanol/n-hexane. The electrocatalytic performance of these nanoparticles was studied by cyclic voltametric and chrono amp metric measurements which show that these have good stability for ethanol oxidation in alkaline media. ‘The La/Cd BNPs has been synthesized using micro-emulsion method and used for degradation of organic pollutants”(Sharma et al., 2015).

2.7 Hydrothermal method

Although nanoparticles are formed under the influence of high temperature nearby 470°C and pressure under 300MPa.The method allows the dilution of mechanisms which are normally non- soluble under normal situations. The properties of the resultant nanoparticles which is depend upon the pH, temperature and pressure of the medium. Then also this method can be useful because it will help in monitoring the crystal growth. Advantage of this method is production of high yield and will get pure products. Moreover to this, Drawbacks of this method include the high apparatus cost and it is not probable to monitor the development process of crystal. Zeolites and nanoparticles of Lead telluride have been synthesized by this method.

2.8 Chemical reduction method :-

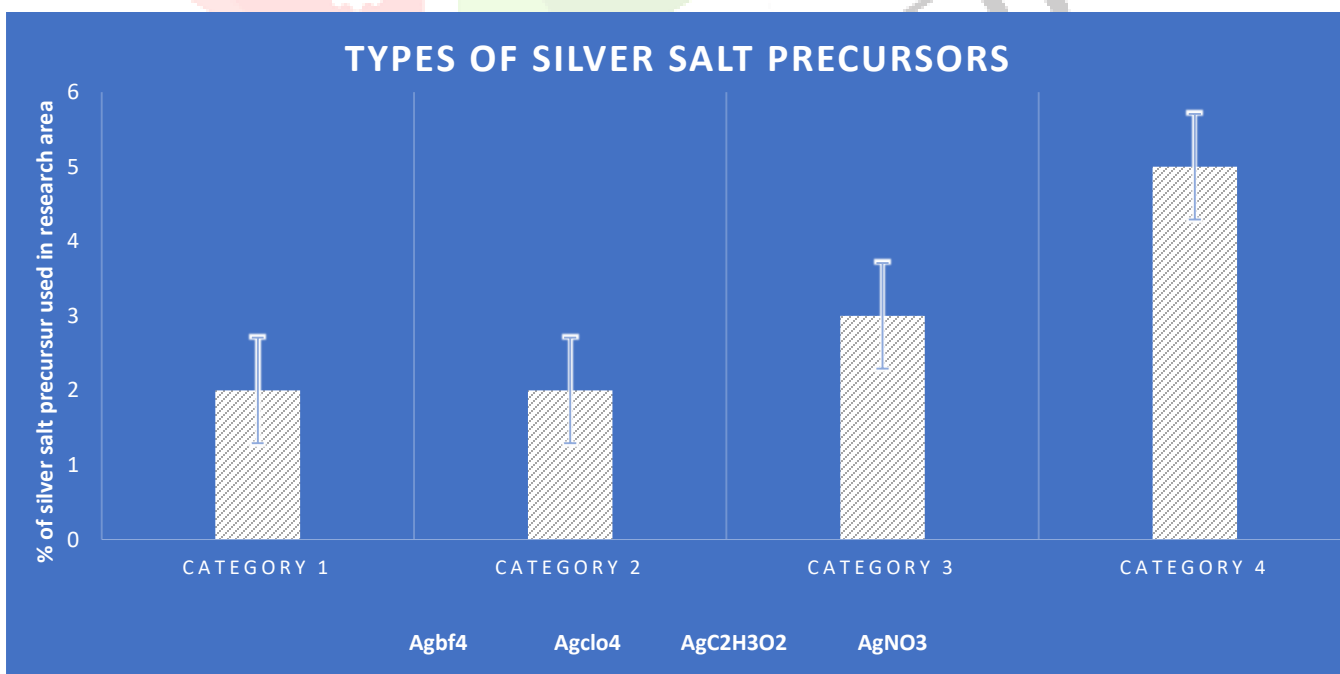
Chemical reduction method is a vary common and simplistic method to deposit of metal NPs into graphene which is include a metal salt and precursor agent. It is produces metal nanoparticle in the zero valent state. This includes two process it’s called as reduction and interaction between the metallic and polymeric types function. Different reducing agent in this process used and it take a short time and area so researchers favorable & likable process. Since its process done in labs , this is most common reason to use this process by researchers. This chemical reduction method include of three simple steps first is reduction of metallic salt by reducing agent, second is stabilization of ions or complex and the third or last is controlling of the size by the capping agent. When this process start and occur the precipitate which is the metallic atoms from its salt solution and after that nucleates. overall chemical reduction synthesis technique consists of three elements, which are metal salt precursor, reducing agent, and stabilizer or surfactant. Sometimes, solvent may be introduced to solubilize the metal salt and other chemicals that involved in the synthesis process.



In above graph fig2. dG is the free energy change or the free energy of new volume formed, r is the radius of the nuclei, the overall free energy has a positive maximum value at a critical size (r^*), which is called maximum free energy (dG^*). dG^* maximum free energy is the activation energy for nucleation and therefore must be prevailed during nucleation procedure. Nuclei bigger than critical size will more reduced their free energy for subsequent growth into nanoparticles. And lower the free energy designates the nanoparticles growth process have become natural or spontaneous process. As well, the critical nuclei size r^* can be gained by setting $d\Delta G/\Delta dr = 0$. which is a proven equation and it has been derived (Burda et al. 2005). Any nuclei with $r > r^*$ will be grown to nanoparticles and any $r < r^*$ will be dissolved. Kinetic rate is a good theory to explain the nuclei developing and dissolving process.

“Tolaymat et al. (2010)” had performed an analysis on type of Ag salt precursors that had been Fig. 3. They (Tolaymat et al. 2010) found that silver nitrate ($AgNO_3$) is the most widely used Ag salt precursor compare to others as shown in Fig. 2

$AgNO_3$ is a commonly used precursor due to its low cost and chemical stability (Lee et al. 2007), although silver acetate, silver citrate, silver sulfate, silver perchlorate, and silver 2-ethyl hexonate have also been used (Manikam et al. 2011). Ag salt precursors are mainly used to produce ionic silver, which can be reduced and precipitated to form silver atoms, clusters, and nanoparticles later. However, appropriate reducing agents should be chosen for the reduction before precipitation can happen, and thus it plays a key point in the synthesis of Ag nanoparticles.



According to Tolaymat et al. (2010), reducing agent is either a chemical agent, plant extract, biological agent, or irradiation means that is used to reduce Ag ions during production of Ag nanoparticles. Sodium borohydride (NaBH₄) was first utilized as reducing agent in 1979 by Creighton et al. (1979). They succeed in preparing Ag nanoparticles by reduction of AgNO₃ with rapid mixing and vigorous shaking of NaBH₄ (Creighton et al. 1979). After that NaBH₄ also started being widely used until today. Song et al. (2009) has successfully produced Ag nanoparticles by slowly dropped AgNO₃ into NaBH₄ in the presence of a stabilizer named sodium dodecyl sulfate (SDS). And after that similarly above process to synthesis Ag nanoparticles with NaBH₄ as the reducing agent, but then dissimilar stabilizers have been used. In “Li et al. (2003) work; AgNO₃ and mercapto acetic acid were added into a triply distilled water with stirring condition. Next, KI was slowly dripped into the above mixture with vigorous stir and a light yellow-green AgI colloid was formed. NaBH₄ was then added into the AgI colloid, and Ag nanoparticles were finally formed. The overhead procedure was also operated by Zhao et al. (2006a, b) except mercapto sulfonic acid and NaI were used instead of mercapto acetic acid and KI correspondingly. The finding of their works is common, i.e., spherical Ag nanoparticles with narrow distribution of sizes and shapes were obtained. NaBH₄ is the most widely used reducing agent in synthesis of Ag nanoparticles as reported in many other works (Shon and Cutler 2004; Limsavarn et al. 2007; Van Hyning et al. 2001a, b; Doty et al. 2005; Zou et al. 2006; Medina-Ramirez et al. 2009; Liu et al. 2010, 2012b; Pinto et al. 2010; Vorobyova et al. 1999; Angelescu et al. 2012; Radziuk et al. 2007; Krutyakov et al. 2010; Lee and Meisel 1982). The overhead declaration is also accepted by Tolaymat et al. statistics work (Tolaymat et al. 2010). However, the volume of NaBH₄ being used is always in excess for the reduction of Ag salts (Creighton et al. 1979; Radziuk et al. 2007; Angelescu et al. 2012; Liu et al. 2007; Song et al. 2009). This is because when a small amount of NaBH₄ is used, the boron hydroxide being produced through hydrolysis of borohydride (Eq. 3) tends to be adsorbed onto the surfaces of Ag nanoparticles (Song et al. 2009; Liu et al. 2007; Davis et al. 1962).

This reduces the electron density of surfaces and causes profound aggregation of Ag nanoparticles. Excess amount of NaBH₄ may produce a thick layer of BH₄⁻, which serves as an electrostatic barrier and prevents the Fig. 2 Analysis of Ag salt precursors reported in Ag nanoparticles synthesis (Tolaymat et al. 2010).

Table 1:- Summary combination of Ag salts, reducing agents, stabilizers, surfactants, and particle sizes been reported in Ag nanoparticles synthesis via chemical reduction route:-

<u>Ag salt precursor</u>	<u>Reducing agent</u>	<u>Stabilizer/surfactant</u>	<u>Reported size</u>
Silver nitrate	-	trisodium citrate & Ascorbic acid	35-38 nm (G. suriati, M. muriatti, and A. azizam) in 2014
Silver nitrate	Sodium borohydride	-	1-50 nm (Creighton et al. 1979) 20-180 nm (Vorobyova et al. 1999)
-		SDS	30-40 nm (Song et al. 2009)
		Laponite	<10 nm (Liuet al. 2007)
		Mercaptoacetic acid	17 nm (Li et al. 2003)
		Mercaptosulfonicacid	8 nm (Zhao et al. 2006a,b)
		Alkanethiolate	2-5 nm (Shon and Cutler 2004)-
		Poly(styrene sulfonate-co-maleic)	(limsavarn et al. 2007)
		peptide	5.8-20.8 nm (Doty et al. 2005)
		thioalkylated poly-(ethylene glycol)	4.3-6.3 nm (Doty et al. 2005)
		Mercaptoethanesulfonate	3.2-3.8 nm (Zou et al. 2006)
		gum arabic	2.5-4.3 nm (Medina-Ramirez et al. 2009)
		Poly(N-isopropylacrylamide)	8-11 nm (liu et al. 2012b)
		sodium citrate	4.6-5.0 nm (Pinto et al. 2010)
		pluronic F127	8-16 nm (Angelescu et al. 2012)
		sulfonatedpolyaniline	2-4 nm (krutyakov et al. 2010)
			56-71 nm (Dong et al. 2009)

	Sodium citrate	-	35-100 nm (Tan et al. 2003) 60 nm (Zhao et al. 2006c) 100 nm (Sileikaite et al. 2006) 10-20 nm (Ratyakshi and chauhan 2009) 17-94 nm (Lie et al. 2007) 10.0-31.6 nm (medina-ramirez et al. 2009) 2-11 nm (wang et al. 2008)
	Hydrazine	PVP Gum arabic	
	(1) Hydrazine hydrate	SDS + isopentanol	8-50 nm (Guzman et al. 2009) 60-120 nm (nersisyan et al. 2003) <20 nm (Szczepanowicz et all. 2010) 15 nm (khan et al. 2009)
	(2) Hydrazine dihydrochloride	SDS Cetyltrimethylammonium bromide (CTAB) Triton x-100 Tetra-n-butylammonium bromide (tbab) + 1-dodecanethiol PVP PVP Tween20	- 3 nm (zhang et al. 2011a) 20 nm (Khanna et al. 2005) 50 -100 nm (zhang et al. 1996) 50 nm (seo et al. 1996) 40-70 nm (nickel et al. 2009)
	Ascorbic acid	-	
	formaldehyde	Daxad 19	14-42 nm (sondi et al. 2003) 20-100 nm (suber et al. 2005) 10 nm (al-thabaiti at al. 2008) 50 nm (al-thabaiti et al. 2008) 31-73 nm (qin et al. 2010) 5-21 nm (chen et al. 2007) 10-20 nm (nersisyan et al. 2003) 7-20 nm (chou and ren 2000) 15 nm (hdu and wu 2010) 30 nm (yu and zhang 2010) 7.99 nm (hsu and wu 2010) 2.7 nm (hsu and wu 2010) 4.5-56 nm (lah and johan 2009), lah and johan 2011) 153 nm (ullah et al. 2006)
	Glycerol(alcohol gp)	SDS CTAB Sodium citrate Oleylamine SDS PVP	
	Amine	CTAB TSA TEA Daxad 19	
	(1) Aniline	m-phenylenediamine (m-pda)	10-30 nm (khan et al. 2011) 7-10 nm (yang et al. 2011)
	(2) Hydroxyl-amine hydrochloride	CTAB Dodecylbenzenesulfonic acid (DBSA)	50- 100 nm (lundahl et al. 2008)
	(3) Triethanol amine	EDTA	24 nm (rao and Trivedi 2005, 2006)
	(4) Hyper-branch-poly-amidoamine	Stearic acid	4-14 nm (zhang et al. 2008)
	Tannic acid	-	18-30 nm (dadosh 2009)
	Gallic acid	-	7-89 nm (Martinez-castanon et al. 2008)
	ammonia	Pyridinium di-n-hexaoctyldithiophosphate (pyDDp)	20 nm (sun et al. 2003)
	N,N'-dimethyl-formamide	-	7 nm (patakfalvi et al. 2008)
	Saccharides	B-cyclodextrin Cholic acid	4 nm (patakfalvi et al. 2008)
	(1) Glucose	-	40-80 nm (janardhanan et al. 2009)

		-	44-53 nm (panacek et al. 2006)
		SDS	10-50 nm (nersisyan et al. 2003)
	(2) Dextrose	PVP	20-80 nm (wang et al. 2005)
	(3) Lactose	PVP	22 nm (lu and chou 2008)
	(4) hyaluronan	-	35-280 nm (panacek et al. 2006)
		-	7-40 nm (xia et al. 2011)

Table 2:- Classification of stabilizers

Group	Stabilizer/surfactant
Polymer	SDS, PVP, PVA, Dax ad 19, poly(styrene sulfonate-co-maleic), peptide, poly(N-isopropylacrylamide), Pluronic F127, sulfonated polyaniline, Triton X-100, Tween 20, pyridinium di-n-hexaoctyldithiophosphate, β -cyclodextrin
Acid	Mercaptoacetic acid, mercaptosulfonic acid, sodium citrate, TSA, TEA, dodecyl benzenesulfonic acid, ethylenediaminetetraacetic acid, stearic acid, cholic acid, poly(L-glutamic acid)
Amine	Oleyl amine, m-Phenylenediamine, amino silane,
Bromide	CTAB, DTAB, TTAB, TBAB
Ligand	Alkanethiol ate, thiogallate poly-(ethylene glycol), mercaptoethane sulfonate

If we compared the stabilizers in (Table 2) then we can said that polymer is the most used stabilizer if compared to others, but this fight is too general because not all polymeric stabilizers recorded in Table 2 are regularly in used. So this segment therefore intentions to specific review on the most common used stabilizers in Ag nanoparticles synthesis.

the usage of PVP as stabilizer in their synthesis works. So their work initiate that PVP not only uses for stabilizing Ag nanoparticles but also plays an important role in controlling the size and shape of Ag nanoparticles. Zhang et al. (1996), Lu and Chou (2008) noticed that PVP will be absorbed onto Ag surface during synthesis and then provides a protective barrier for the particle. And the protection barrier can inhibit the inter-diffusion between nanoparticles, as well as between nanoparticle and suspension; therefore, it is very effective against accumulation. Kim (2007), Chou and Ren (2000) reported that increasing the PVP concentration tends to produce smaller Ag particles, but appropriate amount should be added. It is because too much PVP will slow down the reduction rate of Ag ion into Ag atom, and thus not suitable for practical uses (Chou and Ren 2000).

the previous explanation about protective barrier also applicable for PVA case (Patil et al. 2012; Zielinski et al. 2009; Khanna et al. 2005; Chou and Ren 2000), but increasing the concentration of PVA does not lead to the reduction of Ag nanoparticle size (Patil et al. 2012). Therefore, PVA only serves for preventing Ag nanoparticles from agglomerate. Furthermore, Chou and Ren (2000) did a comparison between PVP and PVA; they found PVP is somewhat better than PVA for protecting Ag particles from agglomeration. In addition, cetyltrimethylammonium bromide (CTAB) (Khan et al. 2009; Al-Thabaiti et al. 2008;

Table 3:-

Ag salt precursor	Reducing agent	Stabilizer/surfactant	Reported size
Silver chloride	Hydrazine	PVA	10–60 nm (Patil et al. 2012)
Silver citrate	Hydrazine	PVA	60- 67 nm (Zielin'ska et al. 2009)
Silver citrate	Ascorbic acid	PVP	36–82 nm (Zielin'ska et al. 2009)
Silver 2-ethyl hexanoate	Dimethyl sulfoxide	Sodium citrate	4.4 nm (Rodri'guez-Gattorno et al. 2002)

2.9 The constituents of silver and sulfur at different different time notice by (Zhang et al. 2011 a) as follow :-

Reaction time	wt of silver in %	wt of sulfur(%)
3	91.11	8.89
5	86.59	13.41
8	79.27	20.73
12	76.56	23.44

a weak plasmon peak centered at 400 nm was observed at low molar ratio of 0.5. The intensity of the plasmon peak at 400 nm was later increased with increasing molar ratios from 0.5 to 15, which indicates much Ag nanoparticles were being produced at higher molar ratio of NaBH₄/AgNO₃. Moreover, the broad plasmon peaks obtained at low molar ratios of NaBH₄/AgNO₃ were actually confirming to the aggregation of Ag nanoparticles. Conversely, the narrow plasmon peaks obtained at high molar ratios of NaBH₄/AgNO₃ were confirming to the well dispersion of Ag nanoparticles. In conclusion, NaBH₄ can serve not only as a reducing agent but also as a stabilizer, which may protect Ag nanoparticles from aggregation. Sodium citrate, also known as trisodium citrate (Na₃C₆H₅O₇), is another widely used reducing agent in synthesis of Ag nanoparticles.

When we see the history of synthesis then we notice that In 1951 sodium citrate was also first used by Turkevich et al. (1951) for the synthesis of Au nanoparticles. After that this method was then used and refined to work on synthesis of Ag nanoparticles as reported by Li et al. (2007) and Dong et al. (2009). And the researcher (Li et al. 2007) had utilized AgNO₃ and poly(vinylpyrrolidone) (PVP) as precursor and stabilizer, correspondingly. The aqueous AgNO₃ solution and PVP were first mixed and stirred; the mixture was then heated near to boiling temperature and 1 % sodium citrate was added with vigorous stirring. The Ag nanoparticles with size between 17 and 94 nm were obtained, but a major drawback of this method that the product was unstable at room temperature (Li et al. 2007). So this method (Lee and Meisel) has become another projecting method in synthesis of Ag nanoparticles and frequently used by many researchers (Tan et al. 2003; Can amares et al. 2005; Zhao et al. 2006c; Sileikaite et al. 2006; Ratyakshi and Chauhan 2009).

Ratyakshi and Chauhan 2009; Sileikaite et al. 2006 works also did mention about the use of sodium citrate as reducing agent in Ag nanoparticles synthesis (Wang et al. 2008; Naik et al. 2010; Medina-Ramirez et al. 2009; Guzman et al. 2009; Khanna et al. 2007b).

However, hydrazine hydrate is more frequently being in used as reported by Guzman et al.

2.10 change in ag nanoparticles in different tempreture and PH:-

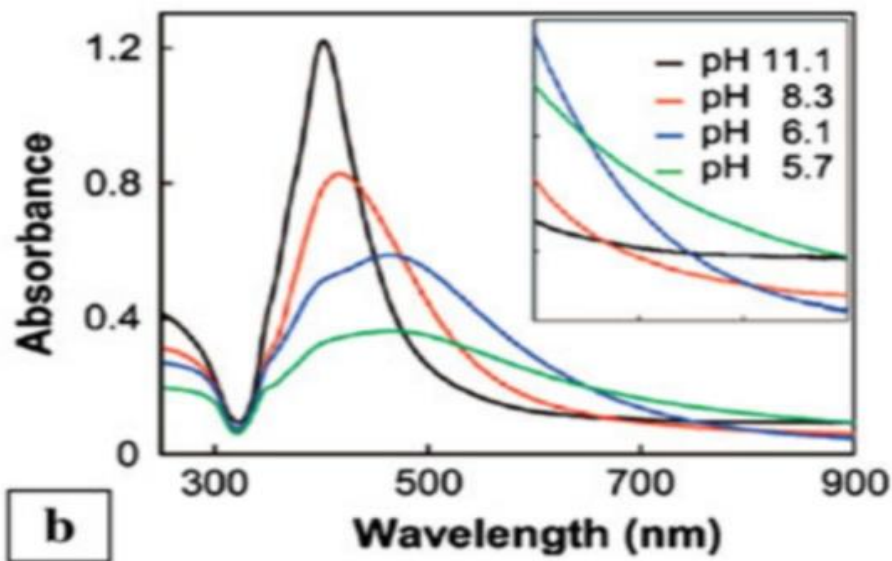
Since dong et al. (2009) have described about changes in Ag nanoparticles on different tempreture and PH because PH of reaction mixture can effect the size and shape of the final Ag nanoparticles.

Which ag nanoparticles synthesized by sodium citrate reduction of AgNO_3 from PH about 5.5 to 11.1.

He found that under high PH , spherical and rod like Ag nanoparticles were formed as a resultant of high reduction rate of precursor. In shortly , when he decrease the PH then triangle and polygon Ag nanoparticles were seen due to slow reduction rate of the precursor. And we can say that average particle size decrease from near of 5.5 to 11.1 , steady with the red shift of the UV absorption peaks (fig.3).

Finally, the observation in reaction 99.7 % of AgNO_3 manage to be reduced to Ag atoms and growth into nanoparticles after 60 min. (Chou and Ren 2000). Simultaneals, many other syntist for example Khanna and Subbarao (2003) also noted the similar data but they only success to reduce 95% of AgNO_3 to Ag nanoparticles. Under 10.0 to 10.5 PH value with alkaline condition were applied then we successfully synthesized 1-30 nm Ag nanoparticles (Khan et al. 2011). We noticed that reducing ability of amino acid tyrosine reacted only at alkaline PH. Although above mention works have show that Ag nanoparticles synthesized are more favorable in alkaline PH medium. But its not apply on all component mixture of reducing agent and Ag salt. It is because of hydrazine, ascorbic acid and NaBH_4 , trisodium citrate were used as reducing agents and their reducing capacity were independent of PH.

The above type result was also supported by other researchers, where we can see higher pH is more favored for Ag nanoparticles synthesis. And in ancient Chou and Ren (2000) used formaldehyde to reduce AgNO_3 and then we found on low PH, the reduction rate would be too slow because PH effect the reduction rate . and on other hand different quantities of NaOH and/or Na_2CO_3 were added to raise the pH of the solution stayed above fig3.



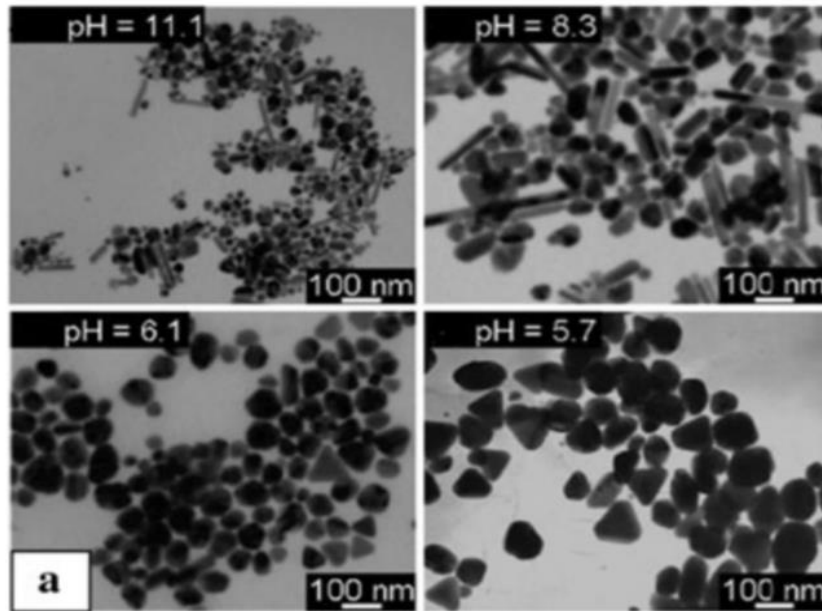


Fig.3. b) show the UV-Visible spectra at different Ph condition for Ag NPs (Dong et al. 2009)
 a) show the transmission electron micrograph at different Ph for Ag NPs (dong et al. 2009)

For synthesis process temperature is play an important role to speed up the synthesis process. But, it is difficult to summarize that all temperatures working in Ag nanoparticles fusion payable to wide range of temperatures being employed in many research works. But when we see heating for two or three times during synthesis were used by investigators and this is vary challenging parts to synthesis time summarize. So on morphology, we explore the effect of temperature on particle outer size and shape .

When we study about many investigators works then we say temperature effect the Ag nanoparticles morphology. In yu and zhang (2010) work three reaction temperature utilized first is 20 degree, second is 40 degree and finally 60 degree. We study that when reaction temperature increased, the particles became smaller in size and undeviating in shape.

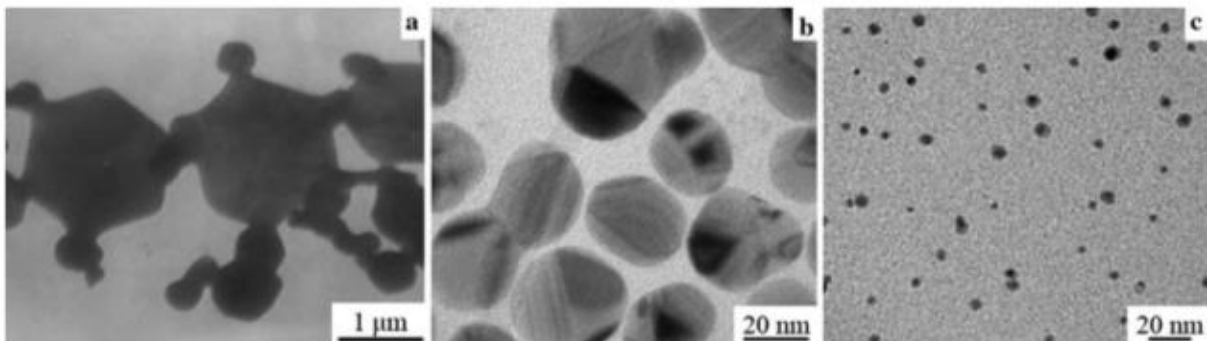


Fig. 4 a) 20°C, b) 40°C, c) 60°C formed TEM images at different temperature for Ag nanoparticles. (Yu and Zhang 2010).

In fig. 4, nonuniform and large size nanoparticles formed at 20 degree and when temperature increase about 40 to 60 degree then we get flaky and spherical shapes particles. i. e. decrease in particles size with increase in temperature. Reducing capability of reducing agent also noticed by (yu and zhang 2010). They said that reducing ability of formaldehyde and capability of CTAB to impede the growth of particles were vary weak at low temperature, and this leads to the formation of large particles. i.e. when temperature were raised about 80 to 120 C then Ag nanoparticles large size will be seen(Luo et al. 2005; lah and johan 2011). And the increment in temperature, the nanoparticles shapes also growth from spherical to polygon. And the above discuss temperature could not apply for all Ag nanoparticles synthesis process, because changed combination of reducing agents and Ag salts will show changed reducing capability with temperature.

3. Precipitation of Cu nanoparticles by chemical reduction route: -

now in order to discussing synthesis process of Ag nanoparticles & synthesis of cu nanoparticles is much more demanding and difficult because it is fastly oxidise and proceed to CuO, Cu₂O, Cu(OH)₂. Many more literature work shows that Cu nanoparticles via chemical reduction route are less compare with Ag nanoparticles. And reducing agent, stabilizer are systematically noted down as well as Cu nanoparticles synthesis by chemical reduction route will be also summarize and recorded in table.

In which sodium borohydride (NaBH₄) is the mostly frequent used reducing agent in Cu salts reduction. after that Hashemi pour et al. (2011) & Zhang et al. (2009) declared the same usage of NaBH₄ to reduce copper sulfate (CuSO₄) solution in the existence of PVP and uncontaminated nitrogen. In the above process the main difference between their work fields and the solvent being active during synthesis, in their work ethylene glycol and distilled water were used respectively by Zhang et al. (2009) and Hashemi pour et al. (2011). lastly, fine Cu nanoparticles were obtained with ethylene glycol solvent if equated with distilled water solvent because ethylene glycol has a better ability to prevent the oxidation and aggregation of the nanoparticles or nano molecules.

In table 4 : Charts of combinations of precursor, reducing agent, stabilizer for synthesis of cu nanoparticles by chemical reduction route :-

Cu salt precursor	Reducing agent	Stabilizer/surfactant	Reported size
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Table 3: - cu salt, reducing agent, stabilizer or surfactants and the relative particles sizes has been reported in cu nanoparticles synthesis .

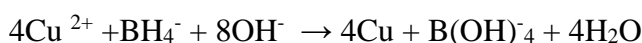
We can see in above table that many more researchers have been reported the method and results of the process. By the help of above table we can easily understand about precursor, reducing agent , stabilizer and precipitate cu nanoparticles size by chemical reduction route.

A small chemical reduction process of Cu nanoparticles :-

Materials of cu nanoparticles synthesis :- CuSO₄.5H₂O (0.1M), Starch (C₆H₁₀O₅)_n (1.2%), ascorbic acid C₆H₁₀O₆ (0.2 M) and sodium hydroxide NaOH (1M) of sigma Aldrich and distilled water.

Synthesis process :- addition of 0.1 M Cu (II) sulfate pentahydrate solution into 120 ml of starch (1.2%) solution with stirring for 30 min. and then 50 ml of 0.2 M ascorbic acid solution is added to synthesis solution with stirring. On the other hand 30 ml of 1M NaOH solution was slowly added in the ready solution with constant stirring and heat at 80°C (for two hours). And colour of solution change yellow to ocher. End of reaction, the solution taken from the heat and settle for overnight and supernatant solution was then discarded continuously. The ppt were separated from solution by filtration and washed by deionized water & ethanol for three times to take out excessive starch and bound with NPs. Ocher color ppt (fig.1) obtained and dry at room temperature. Simultaneously many more synthesis process occurs and Cu nanoparticles ppt size are write down and summarize in above table.

A study of Liu et al. (2012) article shows of NaBH₄ concentration on the formation of Cu nanoparticles. His work shows that CuSO₄ and gelatin were used as Cu salt precursor & dispersant orderly. The size of Cu particles was decreases with the increase of NaBH₄ concentration, but stoichiometric ratio of Cu²⁺ ions to NaBH₄ must maintained at least 4:1 and this equation elaborated below:-



The Liu et al. (2012) reported that at low concentration of NaBH₄, and the resultant product contains Cu₂O, Cu(OH)₂ and Cu nanoparticles. Cu(OH)₂ impurity disappears, if compared to a higher NaBH₄ concentration but Cu₂O impurity disappears only when the NaBH₄ concentration reaches eight times of the stoichiometric value.

CuSO ₄ .5H ₂ O Copper ammonium complex Copper sulfate	Ascorbic acid +NaOH Sodium boro hydride Sodium borohydraide	Starch Hcl Starch Pvp	28-25 nm (A.K., A.R., R.Y., R. Chong) 55-56 nm (N.V. Suramwar, S.r.Thakur, N.T. Katy 2012) 0.8-3.6 nm (zhang et.al. 2009) 25-70 nm (hashemipour et.al. 2011) 37 nm (liu et.al 2012a)
Copper acetate	Hydrazine	Gelatin Ctab + decanethiol -	1-40 nm (Chen et.al. 2006) 50-100 nm (Liu et.al. 2006) 39-69 nm (Kobayashi et.al. 2012)
Copper nitrate	Sodium borohydride Hydrazine	PVP Acetonitrile CTAB + Citric acid	80-130 nm (raut.et.al) <100 nm (Abdullah-Al-Mamun et.al.2009)
Copper chloride	Ethanol Isopropanol Sodium borohydride	CTAB + Citric acid PVP PVA Starch Ligand benzyl diethylene-triamine CTAB	40-70 nm (Kobayashi et.al. 2012) 23-30 nm (Singh et al. 2010) 14-34 nm (singh et.al. 2010) 21-22 nm (singh et.al. 2010) 15-20 nm (Chandra et.al. 2011)
Copper chloride	Hydrazine ethanol	Bis (ethylhexyl) hydrogen phosphate 2-propanol Polyoxyethyleneoctyl phenyl ether + di-octyl sodium sulphosuccinate - PVP + CTAB -	2-20 nm (Athawale et.al. 2005) 50-60 nm (song et.al. 2004) 50 nm (chang et.al. 2011) 10-69 nm (Solanki et.al. 2010) 155-178 nm (Ren.et.al. 2005) <100 nm (Pham et.al.2011) 57-85 nm (Kobayashi et.al. 2011) 48-80 nm (Kobayashi et.al. 2012) 11-12 nm (Das et.al. 2011)

Although NaBH₄ is the most useful reducing agent, which is seen by many researchers for ex. (N.V.Suramwan, S.R.thakur, N.T.Katy 2012, dadgostar et al. 2010, hashemipour et al. 2011). Hydrazine(N₂H₄), SFS and many more another excellent reducing agent used in Cu nanoparticles synthesis. So Pham et al.(2011), and Kobayashi et al.(2011,2012) reported that CuCl₂ solution incorporated with stabilizer CTAB usually used as reducing agent in (2011) Kobayashi et al. said that hydrazine solution was added to CuCl₂ solution that contain CTAB and citric acid under rapid stirring condition at room temperature in air. Kobayashi et al. (in 2011) & A.K.,A.R.,R.Y. and R. Chong(in 2016) have found that by increasing the concentration of hydrazine or citric acid. The Cu nanoparticles occurs in much smaller size & less Cu₂O by product. This type of nanoparticles appears because citrate ions absorbed on the surface of metallic Cu particles. Consequently protecting the Cu particle against oxidation (Kobayashi et al. 2011). And the higher concentration of hydrazine will induced faster reduction rate and so we find finer Cu particle could be formed (Kobayashi et al. 2011,2012).

Now after few years it is modify termed as modified polyol process, in the case of ethylene glycol solvent Zhu et al. (2004a), Zhu et al. (2004b) and yu at al. (2010) have successful synthesized Cu nanoparticles with size of 5-10 nm, 20-80 nm and 30-80 nm respectively. And then in the case of diethylene glycol used as a solvent Tang et al. (2010), Park et al. (2007) obtained Cu nanoparticles in size 10-60 nm & 37-80 nm.

In above solvent features discussion, we can see two similarities firstly, the mixture of Cu salt, solvent and stabilizer is required heat until pre-determined temperature for reaction. And second is PVP was the common stabilizer which is used. So overall reaction of Cu salt is given as :-



If we increase the concentration of reducing agent then also increase the concentration of formed Cu nanoparticles, and particles are smaller but we find that it is limited up to 3:1 for molar ratio of reducing agent and Cu salt. If excess amount of reducing agent being added could result in a very fast reaction leading to a poor size distribution with agglomeration of Cu nanoparticles.

A novel method invented by wen et al. in 2011, which name is two step reduction process for precipitated spherical Cu nanoparticles. In his method CuSO₄ was mixed with EDTA in an aqueous solution. And then Cu²⁺ ions in the aqueous solution were extracted into oleic acid and the resulting synthesis procedure was carried out in organic

segment. And this two – step reduction process can be explained as following :-

- (1) Cu²⁺ ions were firstly reducing into Cu₂O by glucose at 60°c.
- (2) An accurate amount of sodium hypophosphite was added to the solution to reduce Cu₂O to Cu nanoparticles.

Finally well dispersed spherical Cu nanoparticles size ranging between 20-40 nm and had been occurred (wen et al. 2011). Here no need of stabilizer in this method because oleic acid act as both type extractant and surfactant to prevent Cu nanoparticles from agglomeration and oxidation.

After the earlier evaluation, we find all synthesis work which employed for sodium hypophosphite as the reducing agent can produce Cu nanoparticles at atmospheric condition. We notice that here no inert environment is needed during synthesis process.

Sodium formaldehyde sulfoxylate (SFS) (Khanna et al. 2007a, 2008) and ascorbic acid (cheng et al. 2006; Bicer and Sisman 2010; Yang et al. 2006; Blossi et al. 2011) and many other reducing agents used in cu nanoparticles synthesis. In 2006 Cheng et al. has reported the size controlled synthesis of cu nanoparticles from CuSO₄ using SDBS(sodium dodecyl benzene sulfonate, sodium dodecyl sulfate(SDS), and surfactants & ascorbic acid or mixture of them and used polyethylene glycols (PEGs) as a reducing agent. Their recorded data about particle size and size distribution of Cu nanoparticles depending upon type of surfactants as described in table 5 which is summaries by Cheng et al. 2006.

Surfactant	particle size (nm)	particle size distribution (nm)	particle shape
SDS (4g) + PEG-2000 (2ml)	9.5	3-18	Spherical + elliptical
SDS (4g) + PEG-6000 (2ml)	4.1	0.5-9	spherical
SDBS(4g) + PEG-6000 (2ml)	21.8	2-38	spherical + elliptical
SDBS (6g)	3.8	2-6	spherical
SDS (6g)	4.8	2-9	spherical
SDBS (4g) + PEG-600(2ml)	14.0	2-20	spherical
SDS (4g) + PEG-600(2ml)	6.4	3-10	spherical
SDBS(4g) + PEG-2000(2ml)	-	-	strip

On the other way, Bicer and Sisman in 2010 also utilized ascorbic acid to reduce CuSO₄, if stabilizer has been change to CTAB and NaOH was added for control the Ph of mixture. The researchers (Bicer and Sisman in 2010) further noted that the reaction which occurred were Ph dependent and its equation expressed in 9 to 11.



After many more experiment work, we obtained polyhedrons, rods, particles and wires by adjusting the reaction parameters such as reaction concentration, Ph, temperature and so on.

On pleic acid capped Cu nanoparticles has been carried out by Khanna et al. (2008), in this SFS was used to reduce CuCl₂ solution. If we use two different solvents for example ethylene glycol or acetone in synthesis process then the result showed that in acetone has yielded pure Cu nanoparticles with miner Cu₂O impurity. And along with in ethylene glycol has yielding a similar product to acetone and large amount of Cu₂O impurity was obtained too. And PVP was added in the reaction to improve the first reduction of CuCl₂ with SFS in oleic acid and acetone components. Nearly pure Cu and better dispersion nanoparticles were obtained. In the reaction, authors concluded that Cu nanoparticles could effective first capped by oleic acid followed by PVP to avoid agglomeration (Khanna et al.2008). so Cu particle in size of 20 nm could be easily prepared by above mention methods.

Many other reducing agents included ethylene glycol (Ramyadevi et al. 2012), ethanol (Das et al. 2011; Chandra et al. 2011), and diethanolamine (wen et al. 2012). Ethylene glycol, isopropanol and ethanol and many more reducing agents are used as solvents. So polyol process is the specific term for this method.

A novel method was the ramyadevi et al. (2012) synthesized Cu nanoparticles by polyol method. In their method ethylene glycol was used to reduce copper acetate. Tween 80 and ethylene glycol were chosen as stabilizer and

solvent orderly. In 2012 and 2015 respectively ramyadevi et al. and A.K.,A.R.,R.Y.,R.Chong were able to synthesize pure Cu nanoparticles with XRD analysis (fig 9a).

The absorption spectrum of UV-Vis recorded at 580 nm and peak has again attributed to the existence of Cu nanoparticles (fig 9b). above data proved that ethylene glycol has great ability to prevent nanoparticles from oxidation and aggregation. So overall reducing agent, stabilizers and Cu salt being used to produce respective particle sizes, which has been recorded in table 4.

Effect of Ph on Cu nanoparticles synthesis :- since reducing ability of four reducing agents is depending on the Ph of the solution. These are potassium borohydride, hydrazine, sodium borohydraide, sodium hypophosphite and ascorbic acid etc. In 2009 zhang et al. have describe to relate the Ph effect on the final Cu product when sodium borohydride used as a reducing agent and reduce CuSO₄. In 2009 zhang et al. found that at low Ph, strong release of hydrogen bubbles could produce much more amount of Cu nuclei, which tend to aggregate into high agglomerates, while at high PH produced Cu atoms deposit on to the pre-formed Cu nuclei and actually growth to a larger Cu nanoparticles. So resultant PH 11 was the optimized PH for the production of ultrafine Cu nanoparticles. On the other way wu and Chen in 2004, Pham et al. (2011) described the similar reduction of CuCl₂ with hydrazine in aqueous CTAB solution. We could add ammonia in mixture solution for PH adjustment. And they confirmed that PH 10 was critical to produce a pure Cu nanoparticles (Wu and Chen 2004; Pham et al. 2011). So NH₄ was used to adjust PH up to 10 instead of NaOH, because ammonia ion was not only adjust the PH but also used as complex agent to prevent formation of Cu₂O. Although when Ph <10, a low ammonia ions concentration was insufficient for the complex ion of Cu ion and Cu₂O will be formed (Wu and Chen 2004).

In contrast, wen et al. in 2011 had recorded the data about reduction of CuSO₄ with sodium hypophosphite at different PH in order to its optimum PH condition. He seen that a small spherical type products were obtained at PH of 2 to 3. After that many experiments he decided that particles at Ph 3 or 2.5 showed better result when Ph>3, and the product became non-uniform in size and exhibited partly agglomeration to produce bulk product. So finally their work showed that Ph 3 is the important Ph for a spherical Cu particles type product with smaller size and expected dispersion (wen et al. 2011). on the other side, when they using ascorbic acid then the Ph values also play a important role in the reduction of Cu ions. We have also described about Bicer and sisman's work, which is published in 2010, they described the reduction reaction, where Ph is dependent (in equation 9 to 11). And they used NaOH for control the Ph. The size of Cu particles produced was decreased with increase of Ph 3.0 to 6.5 (fig.10).

This is because of increase in reduction capacity of ascorbic acid at high Ph value (in 2010 Bicer and Sisman). Above concept also supported by Wu (in 2007).

Effect of temperature on cu nanoparticles :- temperature is also an important factor which is effect on the on the morphology of Cu nanoparticles. Since when we using NaBH₄ as a reducing agent and PVP as stabilizer then Cu nanoparticles prepared in CuSO₄ solution. This reaction has obviously effected by heating, firstly Cu nanoparticles does not form at 50°C. its formation is start only at 60°C with size of 30 nm. And consequently increase the temperature at 70°C has start to the formation of Cu nanoparticles in size of 70 nm. So this is showed that Cu nanoparticles forms at higher temperature not only larger in size but also poor in dispersion (Hashemipour et al. 2011).

Instead decreasing in temperature from 85 to 60°C has no effect on the size of Cu nanoparticles. In this reaction Cu₂O along with Cu nanoparticles were also obtained at 60°C to 85°C, on optimal (60°C to 80°C) temperature only pure Cu nanoparticles was obtained. While reaction temperature reaches at 60°C for 2.5 h. then submicron wire with diameters of 300-400 nm & lengths up to 10 µm were obtained (Bicer and Sisman 2010). Then again we add sodium hypophosphate into the CuSO₄ solution about at 70°C then we see not instant reaction occurred, thus CuSO₄ remains the same condition and sodium hypophosphate and PVP were used as reducing agent and stabilizer respectively (Tang et al. 2010; Park et al. 2007). Although when reaction temperature continue for 1 hours, then 15 nm Cu nanoparticles was obtained. So further increasing in temperature to 80°C and reaction completing in 20 min. hence obtained particles size will be similar as 70°C. finally we noted that the reaction completion time was shortened to 5 min. and less than 1 min. with increasing the temperature up to 90 to 100 °C. this optimal temperature i.e. 90 and 100°C also accompanied by the reduction process of nanoparticles size in 20 and 25 nm related by Tang et al. 2010. In 2007 Park et al. obtained the 45 nm to 53 nm Cu particles in size and at 40°C to 200°C respectively. From various concepts , our conclusion is that a relatively low temperature the obtained particles size is relatively

small, uniform and good dispersion phase. And at high temperature, the particle size becomes larger, poor in dispersion and non-uniform. This is explained by the reduction rate of Cu^{2+} ions increases with an increasing of the reduction temperature. And the rate of nucleation and particles growth are acceleration with the rise of low temperature to high temperature. As a resultant at high temperature, the particles becomes larger, broad size particles distribution with agglomeration. Particles can not cover the surface of Cu nanoparticles instantly.

Synthesis of Ag-Cu alloy nanoparticles via chemical reduction :- now here we discuss about Ag-Cu alloy synthesis method. Ag-Cu NPs with different different bimetallic proportion were prepared in chemical co-reduction of the salt of the respective metals by using hydrazinium chloride as a strong reducing agent in aqueous solution. We can use NaOH as a rate-controlling agent (Hesham R. Tantawy, A.a.Nanda, Ahmad Baraka, Mohamed elsayed in 2021). The composition of prepared sample elaborated below in the table :-

In Varied proportion Ag-Cu alloy bimetallic samples were prepared by H.R.Tantawy, A.A. Nada, A.Baraka et al. Table 7:-

sample	$\text{AgNO}_3(\text{g})$	$\text{CuSO}_4(\text{g})$	Ag:Cu
Ag	0.68	-	4:0
Ag ₂₅ Cu ₇₅	0.51	0.25	3:1
Ag ₅₀ Cu ₅₀	0.34	0.50	2:2
Ag ₇₅ Cu ₂₅	0.17	0.75	1:3
Cu	-	1.00	-:4

This method actually equality of metals distribution with particles. We characterized the sample by SEM-EDX, XRD and TEM to expose their morphological, crystallin and elemental structure. Here more important line is that Ag-Cu NPs samples were applied for reductive along with oxidative degradation of anionic and cationic dyes. Generally we saw that Ag-Cu have well-organized degradation act for both cationic MB and anionic MO dyes. In this synthesis method each sample prepared by aqueous sample of Cu and Ag precursor. And respective amount of salt (AgNO_3 and CuSO_4) in distilled water (40ml) maintain the molar intensity constant. Then solution was heated at 90°C with vigorous stirring. Aqueous solution of hydrazinium chloride (0.45g/10ml DI H_2O) and NaOH (0.64g/10 ml DI water) were added and at the same time into salt solution. The reaction continue until effervescence stop. This step takes about an hour. Resultant the precipitate NPs were washed 5 times with DI water, then three Ag-Cu bimetallic sample were prepared synthesized Ag₂₅-Cu₇₅, Ag₅₀Cu₅₀, Ag₇₅Cu₂₅ with two monometallic sample. Presented in above table by (Hesham R.tantawy, Amar A. nada, Ahmad Baraka, Mohamed A. elsayed in 2021).

In their sample characterization show the two column, in fig. 5 first column side shows the SEM picture and second side shows the corresponding mapping. in this picture Ag sample shows the fused spherical like nano-particles. Ag₇₅Cu₂₅ sample shows fused rice-like nanoparticles, & obtain Ag to Cu ratio is 73:27 according to EDX analysis. Fig. Ag₅₀Cu₂₅ sample shows fused spherical like NPs & here Ag to Cu ratio is 51:49 according to EDX detection. Sample Ag₂₅Cu₇₅ shows cubic and spherical like NPs, here Ag to Cu ratio is 24:46 according to sample detection. And Cu sample shows the fused cubic & spherical type NPs. All data of BM samples exhibition a regular spreading of Ag and Cu seeing the functional amplification.

Thus chemical reduction is a vary short time consuming, high purity method. In this type Alloy synthesis, hydrazinium chloride ($\text{N}_2\text{H}_4 \cdot 2\text{HCl}$) a strong reducing agent used in the presence of NaOH by (H. R. Tantawy, A.A. nada, A. Baraka, M. A. elsayed in 2021), hydrazine (singh et al. 2011, 2009; Taner et al. 2011) and NaBH_4 (Bhagath singh, A. samson nesaraj in 2013, wang et al. 2010; Ang and Chin 2005) are the three commonly used reducing agents. Amar a. nada, ahmad baraka, Mohamed a. elsayed (2021) noted that co-reduction of AgNO_3 and CuSO_4 in the presence of hydrazinium chloride and NaOH. And singh et al (2009, 2011) presented the co-reduction of AgNO_3 and $\text{Cu}(\text{NO}_3)_2$ with hydrazine in the presence of PVP or starch. At low concentration $\text{Cu}(\text{NO}_3)_2$ used and get 11-13 nm Ag- Cu alloy NPs. If we increase the concentration of $\text{Cu}(\text{NO}_3)_2$,

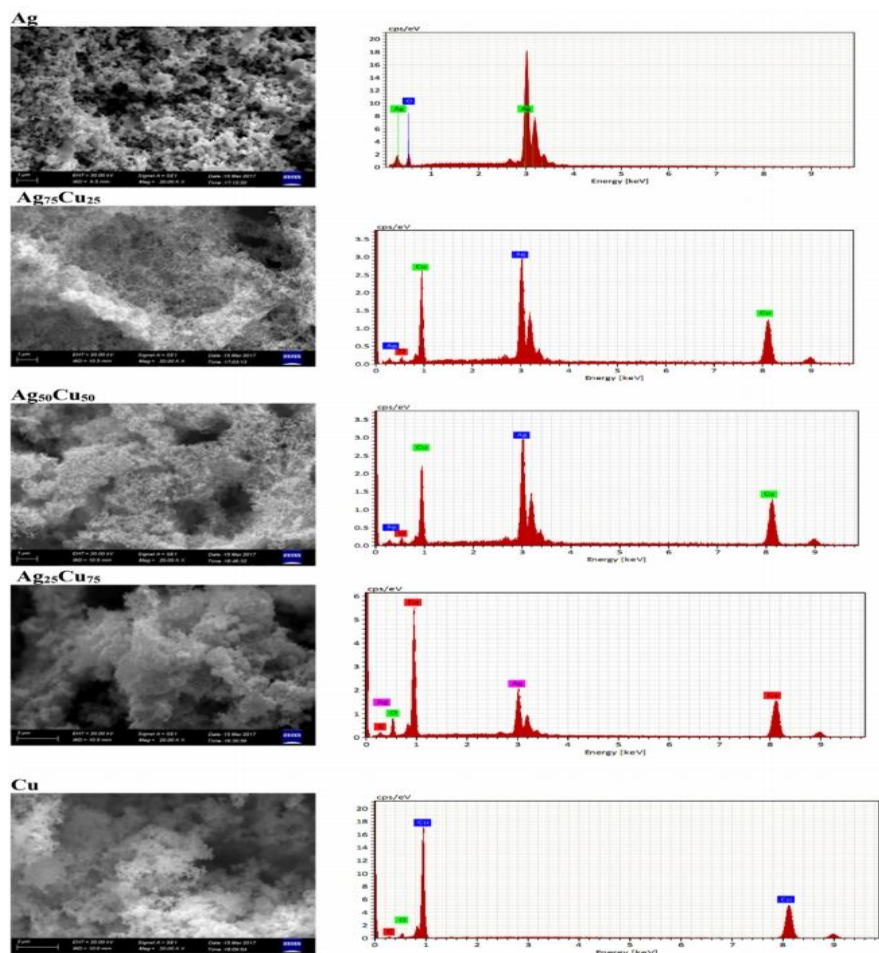


Fig 5. SEM picture and EDX analysis of taken sample by H.R. Tantawy, A.A. Nada, A. Baraka et al. in 2021

and get 11-13 nm Ag- Cu alloy NPs. If we increase the concentration of $\text{Cu}(\text{NO}_3)_2$, Then the cu component also increase in Ag-Cu alloy component by larger in size of nanoparticles. The highest content of Cu which is perceived in Ag-Cu alloy components was only up to 10 at % at 1:5 of $\text{AgNO}_3:\text{Cu}(\text{NO}_3)_2$'s molar ratio.

While in 2010 wang et al. express about a chemical reduction synthesis method which is obtain Ag50-Cu50 alloy nanoparticles with size of 60 to 130 nm. So AgNO_3 , $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ and PVP were dissolved in tetraethylene glycol with stirring. After 30 min, NaBH_4 was added and heated under 270°C for 2 hours. Image 5 show the TEM picture and consistent SED pattern of the Ag-Cu alloy particles which is prepared by above condition in 2010 (wang et al.). the TEM image show the black & white particles in dissimilarity, which means the particles were collected of Ag and Cu. This type image were confirmed that Ag-Cu alloy is present by SEAD based on atomic structure & composition 48.5 : 51.1 ratio of Ag-Cu alloy (wang et al. 2010).

TEM image (a) and SAED pattern (b) of Ag-Cu alloy nanoparticles synthesis in tetraethylene glycol by wang et al. 2010

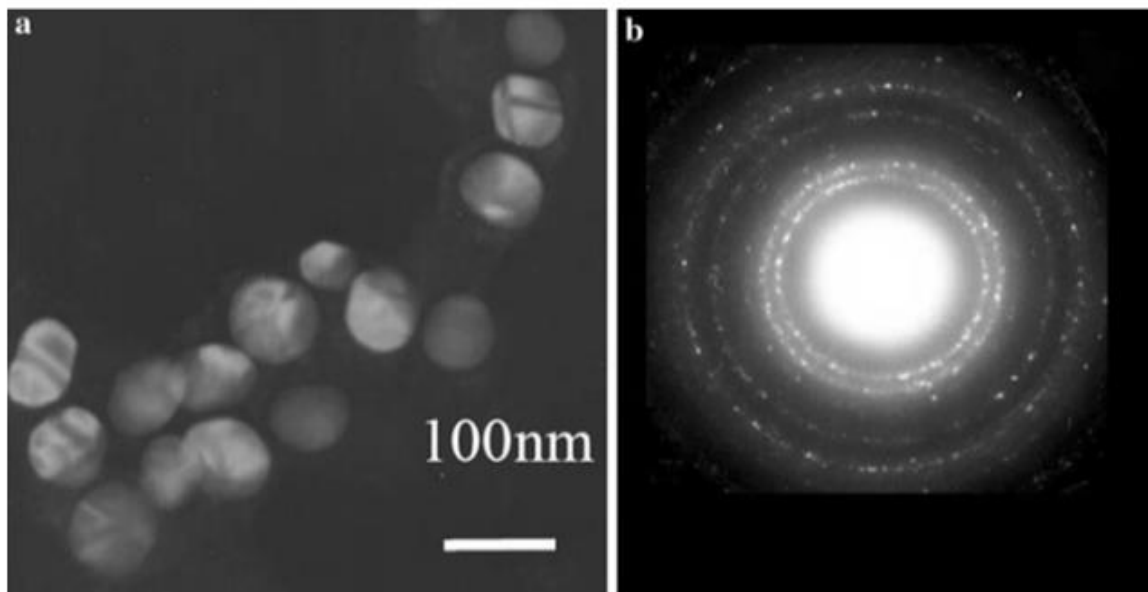


fig. 6 (a) is a TEM image and (b) is SAED pattern of Ag-Cu alloy nanoparticles synthesis in tetra ethylene glycol at 270°C (wang et al. 2010)

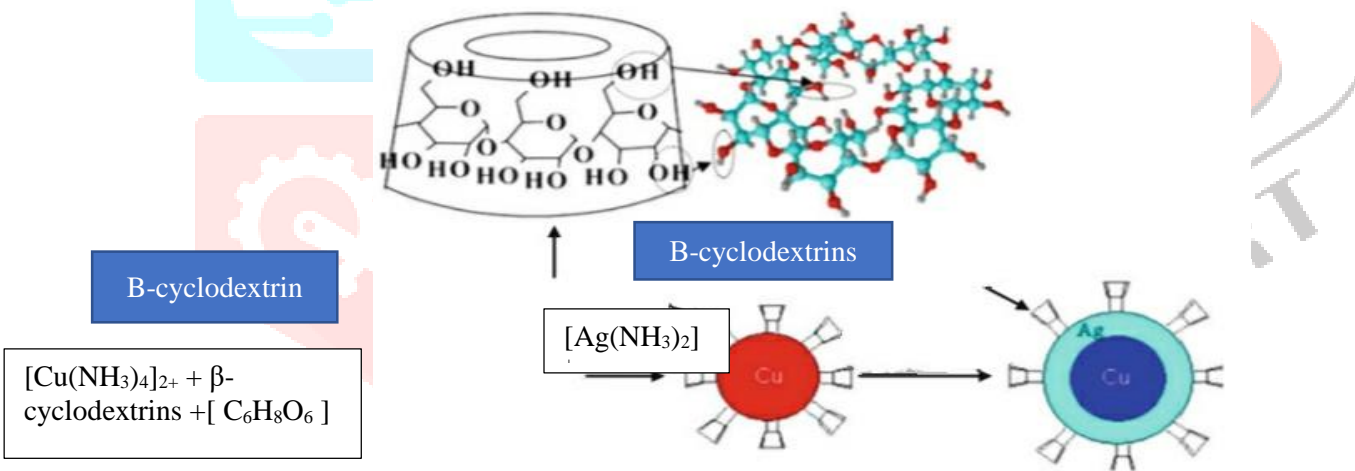


Fig. 7 :- β -cyclodextrins and Ag-Cu alloy formation sequence (Zhao et al. 2010)

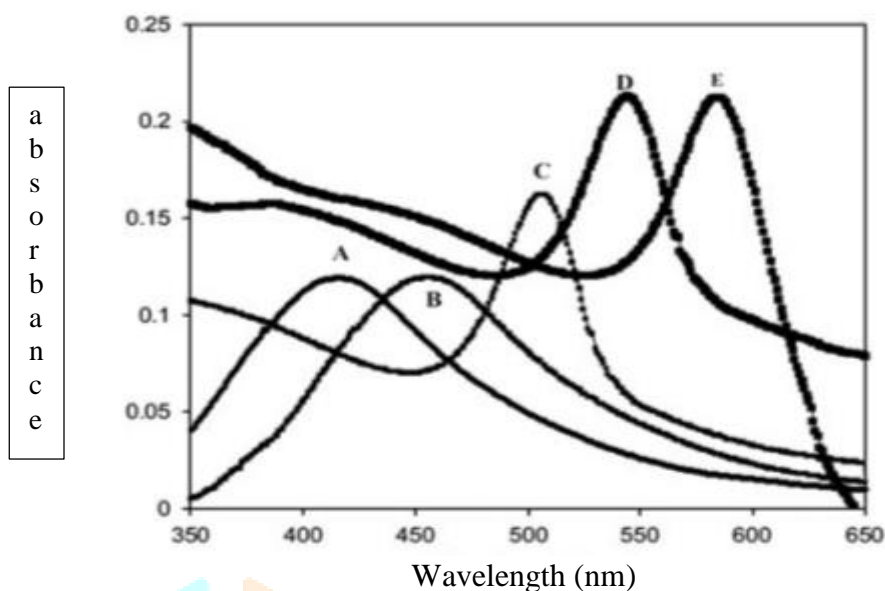


Fig. 8 :- UV-Vis absorption spectra of Ag, Cu and Ag-Cu alloy nanoparticles with mole ratio of Ag/cu i.e. a) 1:0; b) 0.75:0.25; c) 0.5:0.5; d) 0.25: 0.75; e) 0:1 (Valodkar et al. 2011)

R. Capsulata (Hamid reza ghorbani & Roya rashidi in 2017), dextrose (Li et al. 2011) and ascorbic acid (Zhao et al. 2011; valodkar et al. 2011) are three eco-friendly reducing agents used for the synthesis of Ag-Cu alloy NPs. A three step synthesis process expressed by Zhao et al. in 2011. In this method ascorbic acid used as a reducing agent, which is illustrated in fig 7.

Thus, AgNO_3 and CuSO_4 were reacted to make formation of $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ in colloidal forms by adding ammonia in aqueous form. In above reaction final product form as 130-150 nm Ag coated Cu particles forms. The important facts is that β - cyclodextrins played an important role in preventing aggregation of Ag- Cu alloy particles through - OH bonding with Cu particles (Zhao et al. 2011). And another reference is also describing about ascorbic acid reduction with add of powerfull microwave irradiation for 90 s Ag-Cu alloy with size of 20 or about 25nm and has been used for antibacterial activity (Valodkar et al. 2011). Their UV-Vis spectroscopy show the formation of Ag, Cu and Ag-Cu alloy NPs with vary mole ratio of Ag & Cu (fig. 8).

In fig 8 the surface plasmon adsorption peaks appeared at 416 & 584 nm were ascribed to Ag and Cu NPs.

A two step synthesis process also developed by Li et al. in 2010. In this process they used dextrose reduction and PVP stabilization. In this process first time we got Ag NPs by using dextrose to reduce $\text{Ag}(\text{NO}_3)_3$. This Ag NPs assisted as seeds at 85°C for the reduction of $\text{Cu}(\text{NO}_3)_3$. Lie et al. in 2010 also noted that Ag core and Ag-Cu shell were the final structure of NPs.

Instant and new works for future:-

Since chemical reduction is a suitable method Ag, Cu synthesis. It is wide range of shapes and size NPs obtained method. In this chemical reduction method sodium borohydride, hydrazine, ascorbic acid and sodium hypophosphite are the most used reducing agents. PVP, SDS and oleic acid are the most used stabilizers. Overall when we study the various papers of the related topic then we seen that Cu NPs are less widely studied compared with Ag NPs because of fast oxidizing property of Cu. On the other way Ag-Cu alloy NPs synthesis is much more complicated compare to Ag and Cu NPs. In future work, we present the catalogue about right combination of reagent and precursor which can easily produce pure metal and alloy NPs. Most usefull & strong reducing agents like NaBH_4 and hydrazine are the widely used reagents. And sodium hypophosphite has developed as a reducing agents for both Ag and Ag-Cu alloy NPs. Although it is only used for Cu production and ability to produce pure and fine Cu NPs. CTAB also a good stabilizer because its ability to cap both Ag and Cu NPs. And then prevent to growth to a larger size NPs. Ascorbic acid + NaOH with starch or sodium borohydride with HCl and starch are listed. For Ag R. capsulate, dimethyl sulfoxide with trisodium citrate with ascorbic acid are the future trends reducing agents And stabilizer. One line also notice that R. capsulate is a bio friendly stabilizer. Although we always recommended a lower cost synthesis method with good result and ecofriendly for environment. For metal & alloy

NPs synthesis with chemical reduction method does not need for heavy complicated equipment or expensive investment. It was a first attractive point . and secondly, chemical reduction method is vary useful for industry because it is less time consuming, easy for controlling so finally the market price of NPs could be lowered and stabilized.

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3. (Sondi and Salopek-Sondi, 2004),
4. *Streptococcus pyogens* (Nanda and Saravanan, 2009)
5. *Bacillus subtilis*(Rai et al., 2009).
6. *Streptococcus mutans* (Espinosa- Cristóbal et al., 2009).
7. (Biswas et al. 2012; Parak et al. 2010).
8. top-down approach refers to use bulk Ag or Cu mechanically reduces its size into nanoscale (Gates et al. 2005; Niemeyer 2001).
9. bottom-up approach refers to build up of Ag or Cu nanoparticles by self assembly of atoms or molecules (Zhang 2003; Liz-Marza'n and Kamat 2003).
10. (Sharma et al., 2016b; Toshima and Yonieawa, 1998).
11. (Song et al. 2009; Szczepanowicz et al. 2010; Guzma'n et al. 2009; Al-Thabaiti et al. 2008; Nersisyan et al. 2003),
12. (Tan et al. 2003; Can amares et al. 2005; Zhao et al. 2006c; Sileikaite et al. 2006; Ratyakshi and Chauhan 2009).
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14. (Wang et al. 2008; Naik et al. 2010; Medina-Ramirez et al. 2009; Guzman et al. 2009; Khanna et al. 2007b).
15. Hashemipour et al. (2011) & Zhang et al. (2009)