A Study On The Role Of Additives In Non-Cyanide Baths For The Fabrication Of Anisotropic Metallic Nanostructures

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In this study, bath solutions have been prepared for synthesis of gold nanostructures. The role of different additives in bath formulations and their effects on gold nanostructures has been investigated. Synthesis of gold nanostructures through electroless deposition is widely performed using cyanide baths. Here, two non-cyanide gold solutions (bath A and B) are prepared in house and a commercial cyanide gold plating solution (bath C) is used. The 2-Mercaptobenzothiazole that may act as a stabilizing agent is added in Bath A. The Na L-Ascorbate that is a reducing agent is added in bath B. The zeta potential analysis was carried out that exhibited bath B as the most stable formulation. A variety of metallic substrates like silver, copper and nickel have been studied. The surface morphology of metallic substrates was characterized using SEM technique. Anisotropic gold nanostructures of different shapes like star, spherical, dendrite, polyhedral were achieved using non-cyanide baths.

INTRODUCTION

Worldwide consumption of water is growing much more than the population growth. It is doubling every twenty years, twice the rate of population. Major population depends on groundwater as a source of water for drinking and domestic purposes. Irrigation, power generation and industry are other major areas demanding increased water consumption. More than 1.2 billion people lack access to clean drinking water. All economies across the world, whether developed or developing, are severely affected by the water crisis. According to World Economic Forum's Global Risks 2015 report, it is the fourth time that water has made to the annual list that ranks the greatest risks to economies, environments and people. Further, it is the first time that water has moved into the top position for impact [1]. A new analysis from WRI (World Resource Institute) ranks 167 countries for water stress in 2040. A country is considered to be "water stressed" if the average annual amount of drinkable water available per inhabitant is less than 1,700 m^3, "water scarce" if that amount is less than 1,000 m^3 and absolute scarce below 500 m^3 [2].

The major reason behind the scarcity of drinkable water is the dissolution of harmful and poisonous impurities in it, significantly heavy metal ions. Heavy metals are commonly defined as those having a specific density at least 5 times greater than that of water. Such metals include lead, mercury, aluminium, arsenic, cadmium and nickel. Because of their high toxicity, they rank among the priority metals that are of danger to public health. The common symptoms due to prolonged exposure of arsenic experienced by people include skin damage, problems with circulatory system and high risks of

cancer. In India, significant arsenic contamination in groundwater was detected in the year 1983 in West Bengal.

The available arsenic removal technologies need improvement to make them suitable and rational for their large scale effective uses. Some recent development in more efficient techniques for heavy metal ion detection in water has been highlighted in a work that focuses on surface plasmon resonance based optical fibre sensor using conducting polymer and chitosan [3]. Furthermore there have been discussions on different designs and development of Biosensors explaining why bioelectronics, nanotechnology, miniaturization and bioengineering will compete for developing sensitive and selective biosensors [4].

Metal nanostructures are one of the most significant components of nanotechnology due to their physical and chemical properties like the catalytic activity and electron transport that allow them suitable for nano device fabrication. Their significantly higher surface-to-volume ratio makes them an attractive candidate for chemical reactions. Moreover, anisotropic metallic nanostructures are of importance in optical, diagnostic and therapeutic applications [5, 6]. A large variety of bottom-up techniques involving templates or capping agents have been used in the last decade to synthesize various types of anisotropic nanoparticles. Their fine-tuned physical and chemical properties make them ideal candidates for devising new applications. In addition to that the assembly of 1-D, 2-D and 3-D arrays of anisotropic nano materials would introduce completely new properties in the system that might be entirely different from the properties of individual nanoparticles [7]. One of the current challenges in the chemistry of materials is the elaboration of complex nano-scale structures. The conventional method for fabrication of nano structure includes electron beam lithography, nano imprint lithography, focused ion beam lithography, electrochemical deposition techniques etc.

Electro deposition techniques are cost effective and have advantages over the other conventional methods for fabrication of nano structure as mentioned above. The electro deposition techniques include both electroplating and electroless plating techniques. In electroplating of nanostructures, the limiting factor is nanoprobe fabrication and positioning of the same. On the other hand, electroless plating gives more uniform coating thickness as compared to electroplating and therefore, can be considered for the mass production of metal coated surfaces. Among other metals gold plating is extremely important in industries that involve semi-conductors and micro-fabrication. Electroless gold plating involves deposition of a metal B on a metallic substrate A, where ionization tendency of atom A is greater than that of atom B (Figure 1). Cyanide bath is the extensively used for electroless gold plating but its use can lead to toxicity and environmental degradation. Cyanide prevents oxygen absorption by cells and can lead to environmental degradation if disposed inadequately. The stability of the gold cyanide complex induces the reduction potential to occur at very negative potentials, resulting in the co-reduction of hydrogen ions that lowers the plating efficiency and makes the development of electroless plating baths a challenge [8]. Due to safety and environmental concerns the World Health Organisation (WHO) has set the maximum cyanide limit at 0.2 ppm per litre of water. Knowing the significant risks of cyanide usage there are

persistent efforts in developing cyanide-free baths [9, 10].It has also been found that the residual stress of the plated gold can be controlled in non-cyanide baths [11]. Therefore, there is a requirement for the development of more efficient non-cyanide baths that could be used for electroless plating.

Figure 1: Schematic for Electroless plating of metal B on substrate A immersed in bath solution.
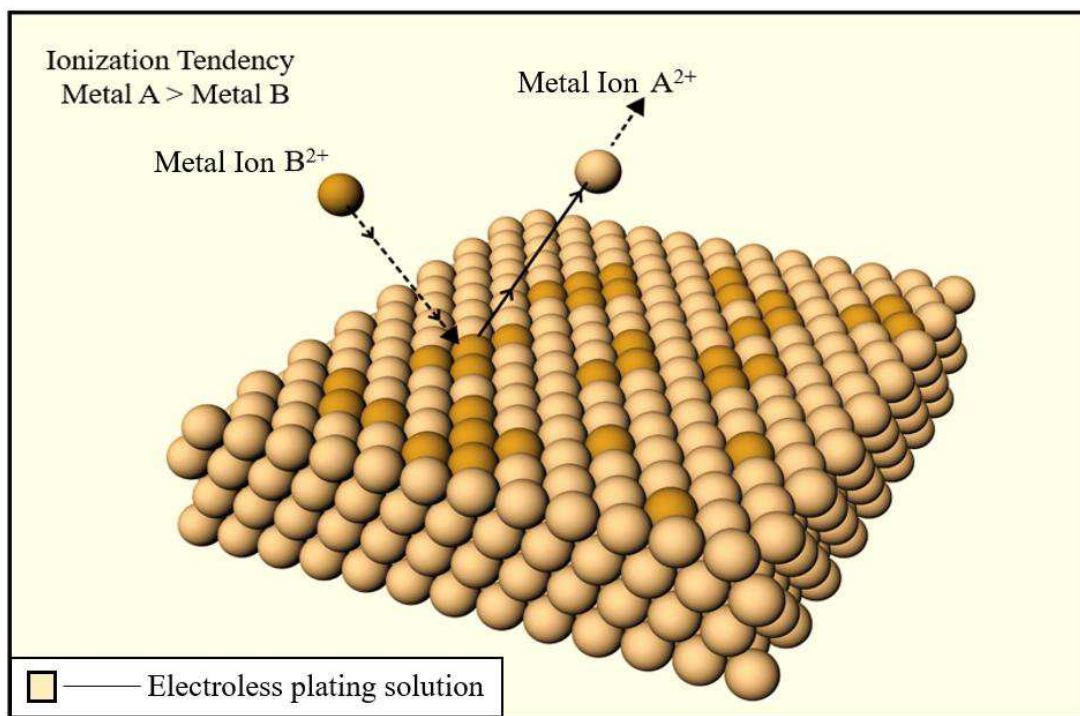
A gold plating bath is aimed to be developed with the absence of cyanide ions for fabricating various substrates like nickel, copper and silver with gold nano structures. The solutions prepared in this study contains both sulfite and thiosulfate as complexing agents for Au (l) while Sodium L-Ascorbate as a reducing agent in bath B and 2-mercaptobenzothiazole (MBT) in bath A as shown in Table I. There have been various studies on the role and characteristics of different bath stabilizing complexes and reducing agent in the non-cyanide baths for efficient electroless gold plating and increased time for bath stability. In a recent experimental analysis on role of addition of different chemicals in the bath it was concluded that the concentration ratio of sulfite to thiosulfate is an important factor controlling bath stability and plating rate, also that 2-mercaptobenzothiazole (MBT) is effective even at very low concentrations. Polyamines such as ethylenediamine and diethylenetriamine have also been reported to increase the plating rate [12]. A recent study was done using polyphenol as a reducing agent and the surface morphology was evaluated by SEM. Catechol, pyrogallol and gallic acid yielded deposited films with good appearance and solderability under the optimized conditions. Among the tested reducing agents catechol was found to be the most suitable as a stable plating bath with a long life [13]. Similarly, Osaka et al. studied about the possibility of electrodeposition of gold from a thiosulfate-sulfite bath for electronics applications and concluded that the bath is stable. The resulted gold deposits had

sufficiently low hardness for use as gold bumps on semiconductor devices. They also observed that the use of high concentrations of the complexing agents and/or the addition of thallium (I) ions decreases both hardness and sulphur content of the deposit [14]. In the present study, non-cyanide sulphite and thiosulphate bath formulations are prepared and electroless gold plating has been performed. The role of different additives in the bath formulations and their effects on gold nanostructures has been investigated. The zeta potential of bath formulations is measured. The metallic substrates such as Cu, Ag and Ni are electroless plated in bath solutions after which the surface morphology of the metallic substrates is characterized using SEM technique.

METHOD AND REAGENTS

In this study, 100 ml of non-cyanide gold solutions (bath A and bath B) are prepared in house and one commercial cyanide gold plating solution (bath C) is used. Composition of bath A and B respectively are given in Table I. Bath C is commercial electroless plating solution that consists of potassium gold cyanide 6 g per litre. Among the above chemicals; Sodium Sulphite - Na_2SO_3 (96 % purity, containing 300 ppm - Chloride and 5,000 ppm potassium), Sodium Thiosulphate Pentahydrate - $Na_2S_2O_3.5H_2O$ (99 % purity), Disodium Phosphate - Na_2HPO_4 (99 % purity) are directly being used in the experiment as purchased by 'Fischer Solution'. Sodium Tetrachloroaurate Dihydrate - $NaAuCl_4.2H_2O$ (99 % purity) is directly being used as purchased by 'Sigma Aldrich', 2-Mercaptobenzothiazole and Sodium L-Ascorbate are directly being used as purchased by Tokyo Chemical Industry (TCI). Any kind of physical or chemical treatment has not been done on the chemicals used in this study.

Table I: Non-Cyanide Bath formulations

Bath – A	Bath – B
Sodium Tetrachloroaurate Dihydrate ($NaAuCl_4.2H_2O$)	Sodium Tetrachloroaurate Dihydrate ($NaAuCl_4.2H_2O$)
Sodium Sulphite (Na_2SO_3)	Sodium Sulphite (Na_2SO_3)
Sodium Thiosulphate Pentahydrate ($Na_2S_2O_3.5H_2O$)	Sodium Thiosulphate Pentahydrate ($Na_2S_2O_3.5H_2O$)
Disodium Phosphate (Na_2HPO_4)	Disodium Phosphate (Na_2HPO_4)
2-Mercaptobenzothiazole	Sodium L-Ascorbate

Every reagent in the bath has a specific role to play depending on its property contributing towards formulating a more stable bath for electroless anisotropic gold nanostructure deposition. In both bath formulations A and B, Thiosulphate-Sulphite mixed ligand ($Na_2S_2O_3.5H_2O$), (Na_2SO_3) acts as a complexing agent. These complexing agents acts as stabilizing agents by regulating deposition speed by blocking a part of catalytic sites and increasing the metallic ion solubility. The 2-Mercaptobenzothiazole act

as stabilizing agent in bath A. The Na L-Ascorbate is expected to influence the crystalline structure of gold nano-deposits in addition to being acting as a reducing agent in bath B and it is also responsible for source of electrons and co-deposited metals.

Amongst the many reducing agents tested, only ascorbic acid, hydrazine and thiourea can serve as the practical reducing agent for the deposition of gold. Evaluation of the bath stability, deposition rate, and deposit appearance, ascorbic acid was selected as the most suitable reducing agent for this bath [15].

The ratio of amount of these chemical reagents in a bath is one of the most delicate factors in deciding the bath stability, plating efficiency and the shape of nano structure deposits. Bath A is formulated by adding 0.398 g of Sodium Tetrachloroaurate Dihydrate (NaAuCl$_4$.2H$_2$O), 4.033 g of Sodium Sulphite, 2 g of Sodium Thiosulfate, 2.8 g of Disodium Phosphate and traces of 2-Mercaptobenzothioazole. In a similar way, bath B is prepared by adding the same amount of the above chemical reagents except that Sodium L-Ascorbate is added instead of adding 2-Mercaptobenzothioazole. All these chemicals are in powder form except Sodium Thiosulphate which is in crystalline form here.

The baths stability is analysed by the zeta potential characterization. Zeta potential is one of the major things that gives an estimation about quantification of the magnitude of charge in the solution. The magnitude of zeta potential gives a measure of electrostatic repulsion between adjacent, similarly charged particles in a dispersion and hence the stability of bath. The surface morphology of different substrates was studied using a scanning electron microscope (SEM).

EXPERIMENTAL

The metallic substrates of nickel, copper, silver and gold of 2 x 2 cm size (Figure 1) are electroless plated in bath solutions for 2 minutes at 60 °C. Clear baths were observed after adding the above chemicals/reagents in their respective masses as shown in Figure 2. The zeta potential of bath formulations is measured using NanoPlus HD-3 particle size & zeta potential analyser. In our experiment it is observed that zeta potential of bath A is +2 mV, bath B is +37.35 mV and bath C is -34.35 mV.

A schematic for electroless plating experiment is exhibited in Figure 3. After this the surface morphology of the metallic substrates are analysed using SEM technique. Equipment used for SEM analysis is SEM Quanta FEG 250, FEI, Netherlands and sputter coating is performed by gold coating unit Leica EM ACE200.

Figure 2: (a) Bare nickel substrate, (b) Bare copper substrate, (c) Bare silver substrate, (d) Bare gold substrate.
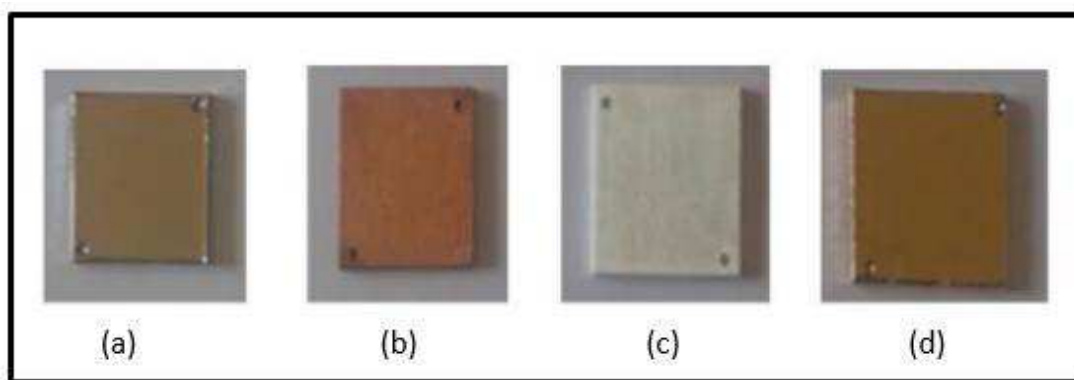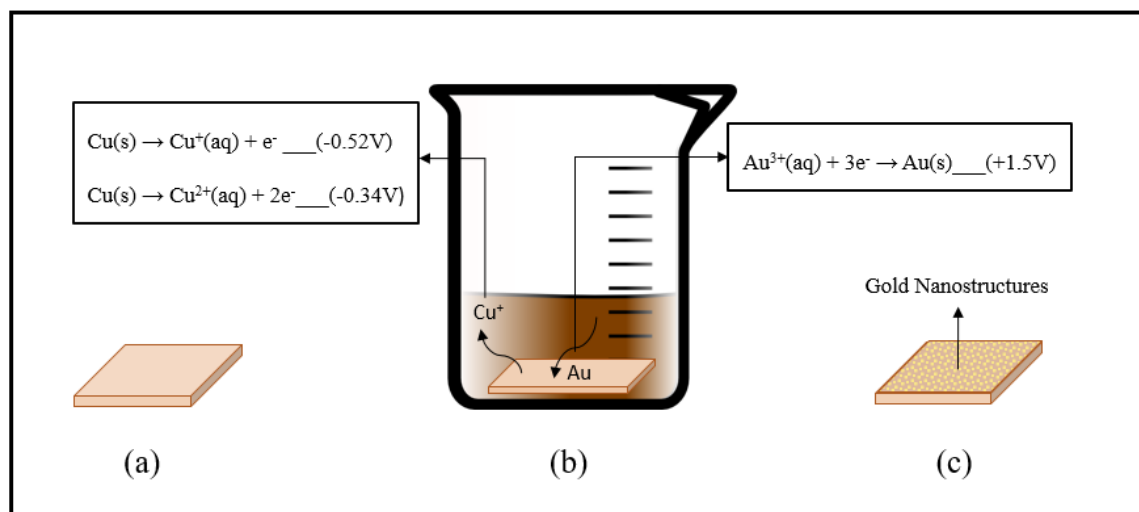
Figure 3: (a) Bath A - 2-Mercaptobenzothiazole. (b) Bath B - Sodium L-Ascorbate.
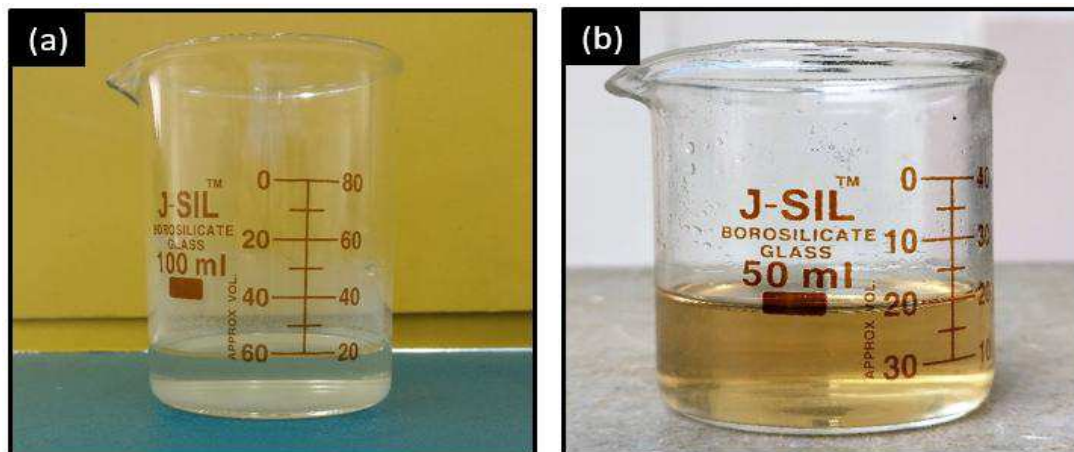
Figure 4: (a) Bare copper substrate (b) Copper substrate dipped in a bath for electroless deposition of gold nanostructures. (c) Copper substrate with deposits of gold nano structures.
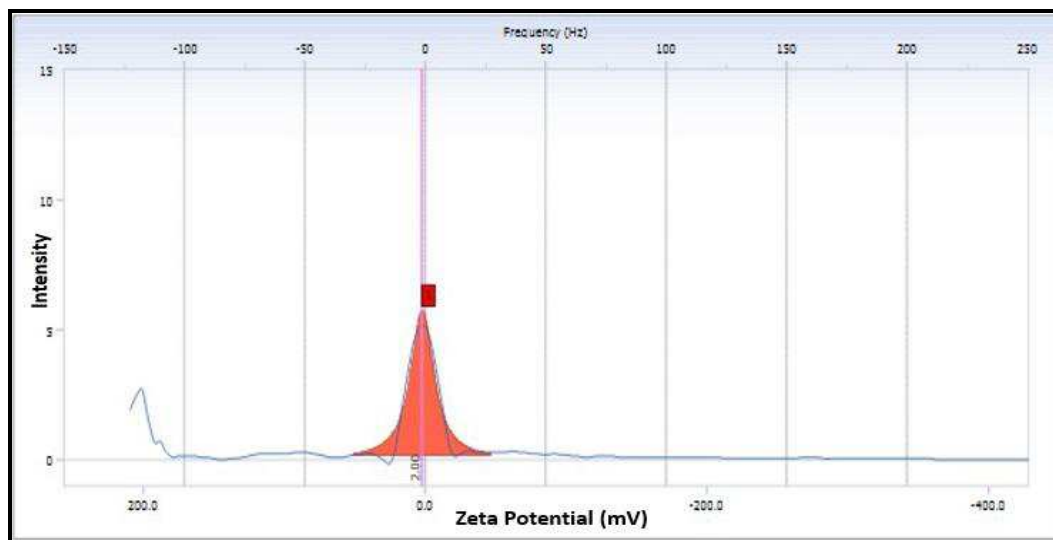

CHARACTERIZATION

Zeta Potential Characterization:

The zeta potential of bath A was found to be 2.00 mV (figure 5) that lies in [0 to ±5] mV, under which the solution is considered to have rapid coagulation or flocculation.
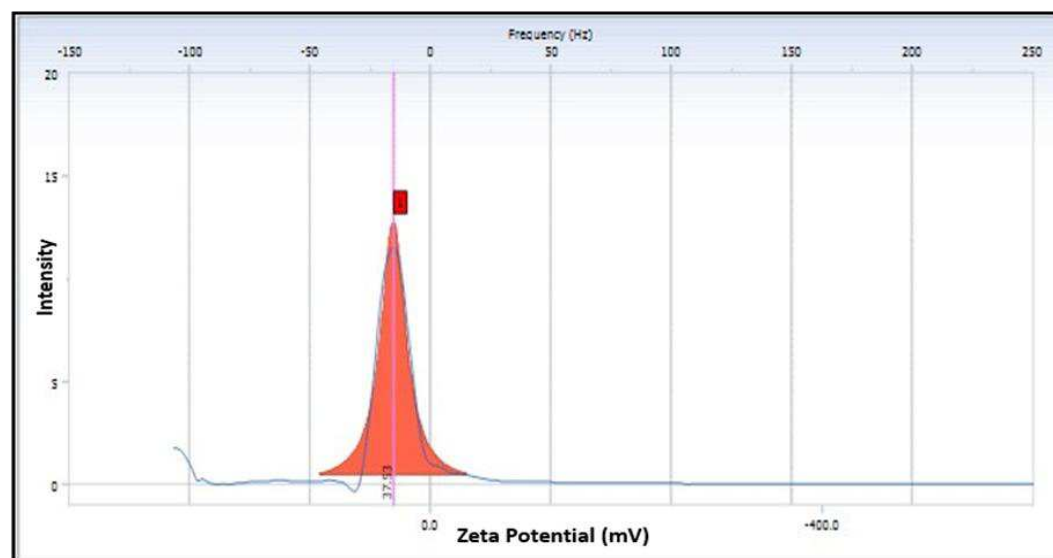
Figure 5: Mobility Distribution - Bath A

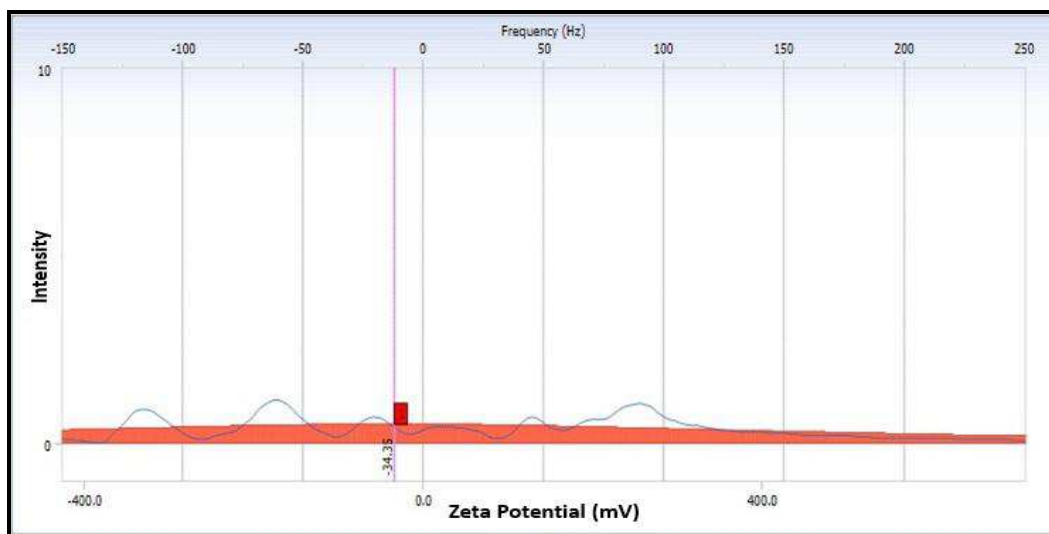| BATH	Peak Frequency(Hz)	Intensity	Half Width (Hz)	Zeta Potential (mV)	Mobility (cm^2/Vs)
A	-1.17	5.72	5.71	2.00	1.557e-005

As shown in figure 6, the zeta potential of bath B was found to be 37.53 mV that lies in [±30 to ±40] mV range. In this case, the solution is considered to have moderate stability.

Figure 6: Mobility Distribution - Bath B

BATH	Peak Frequency(Hz)	Intensity	Half Width (Hz)	Zeta Potential (mV)	Mobility (cm^2/Vs)
B	-15.27	12.74	6.12	37.53	2.927e-004

The bath C solution is considered to have moderate stability as its zeta potential was found to be -34.35 mV (Figure 7) that lie in (±30 to ±40) mV range.

Figure 7: Mobility Distribution – Bath C

| BATH	Peak Frequency(Hz)	Intensity	Half Width (Hz)	Zeta Potential (mV)	Mobility (cm^2/Vs)
C	-12.9	.52	214.73	-34.35	-2.678e-004

SEM Characterization:

After the zeta potential characterization gold, copper, nickel and silver substrates with dimensions 2 cm x 2 cm were dipped in the bath solutions for 2 minutes at a temperature of 60 °C. The solution is agitated continuously with a magnetic stirrer for uniform mixing. The surface morphology of the metallic substrates was analysed using SEM technique.

It is observed that electroless gold plating on copper substrate in the commercial cyanide bath for 2 minutes gives polyhedral shapes of gold nanostrucutre deposits as shown in Figure 8.
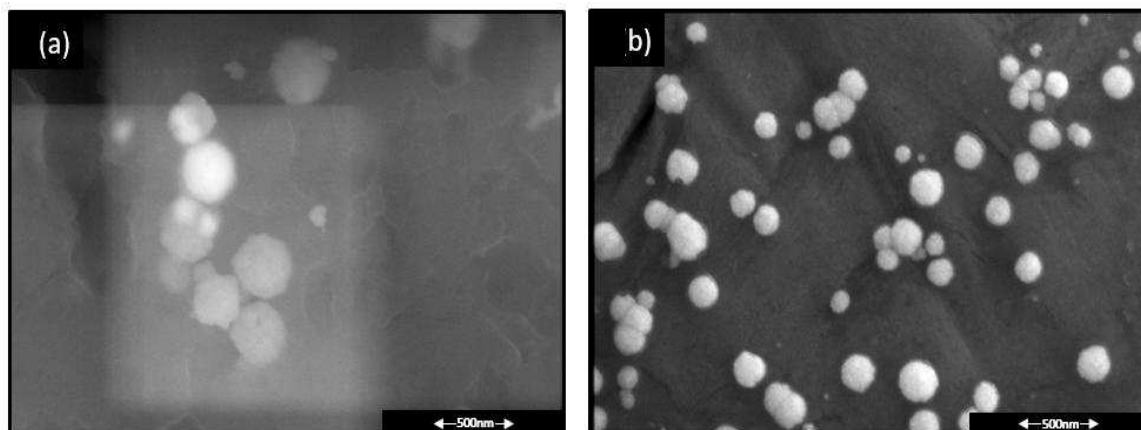
Figure 8: SEM Analysis of (a)Bare gold metallic substrate. (b) Electroless gold plated on copper metallic substrate in the commercial cyanide bath (Bath C).
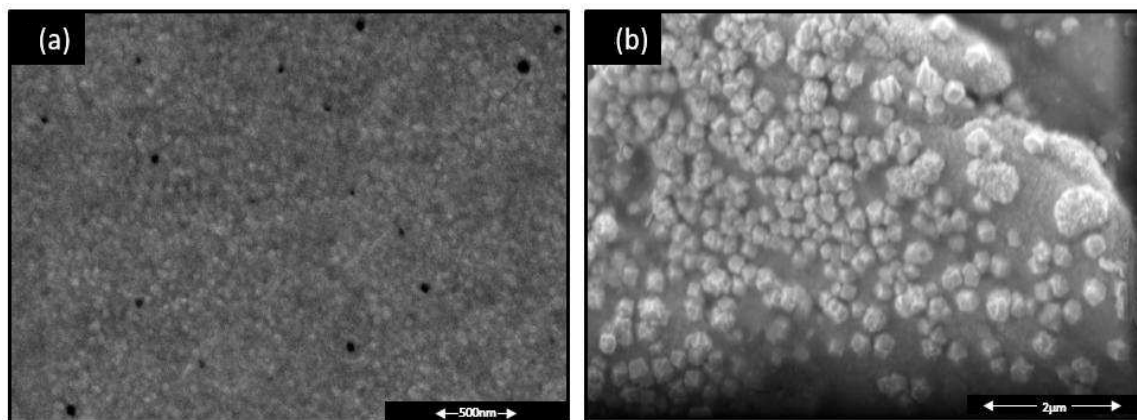
The electroless gold plating on both nickel and copper substrate in bath B - Sodium L-Ascorbate bath for 2 minutes yielded spherical gold nanostructures (Figure 9).

Figure 9 : SEM Analysis: Nickel and Copper. (a) Electroless gold nanostructures deposits on nickel metallic substrate in bath B giving spherical gold nanostructures. (b) Electroless gold plated on copper metallic substrate in bath B giving spherical gold nanostructures .


As shown in Figure 10, electroless gold plating on copper substrate in bath A - 2 Mercaptobenzothiazole for 2 minutes resulted in the growth of flower shape and dendrite shape deposits of gold nano structures.

Figure 10: SEM Analysis: Copper. (a) SEM image of bare Copper metal substrate. (b) Electroless gold plated on copper metallic substrate in bath A - 2-Mercaptobenzothiazole.
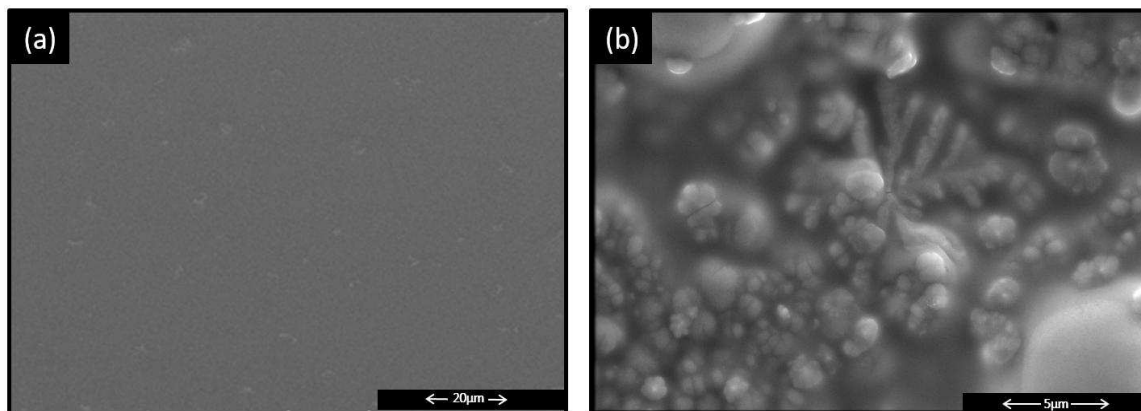
Anisotropic star shaped deposits of gold nano strucutres was achieved after 2 minutes of electroless gold plating on silver substrate in bath A - 2 Mercaptobenzothiazole (Figure 11).

Figure 11: SEM Analysis: Silver. (a) Electroless gold plated on Silver metallic substrate dipped in bath A – 2 Mercaptobenzothiazole giving Anisotropic star shaped gold nanostructures. (b) Figure 10 (a) on a different length scale .
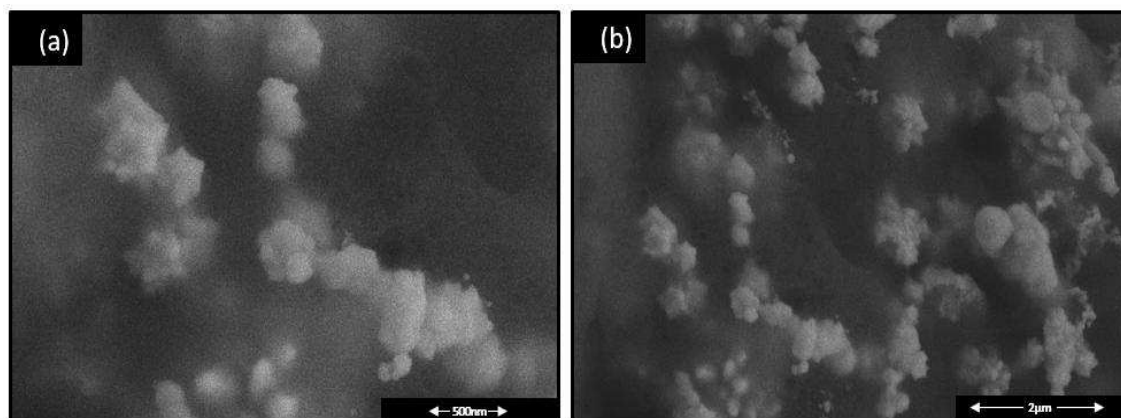
RESULTS AND DISCUSSION

The zeta potential is a key indicator of the stability of colloidal dispersions. For different range of zeta potential stability behaviour of the colloid are categorized accordingly. For zeta potential values ranging from [0 to ±5] mV the solution is considered to have rapid coagulation or flocculation, for [±10 to ±30] mV - Incipient instability, for [±30 to ±40] - Moderate stability, for [±40 to ±60] - Good stability and for more than ±61 it is considered to have excellent stability. From the values obtained from Figure 4, 5 and 6 it can be concluded that bath C and bath B having zeta potential values - 34.35 mV and +37.35 mV respectively are more stable than bath A having a zeta potential value of 2.00 mV as formulated in the experiments. It is also found that the addition of Sodium L-Ascorbate to bath B resulted in a zeta potential of +37.35 mV. The experimental results are in good comparison with the zeta potential values.

At a constant reaction condition of 60 °C and 2 minutes for each experiment, electroless plating in the commercial cyanide bath shows polyhedral shapes of gold nanostrucutre deposits with sides less than 500 nm is formed on the copper substrate. This may have formed due to a capping agent present in the commercial cyanide gold complex. Almost spherical gold nano structures deposits were observed on nickel and copper substrate when electroless plating is done using bath B - Sodium L-Ascorbate which shows the stabilizing act of the Sodium L-Ascorbate additive. For Au nanocrystals with truncated cubic or octahedral shape, such overgrowth can lead to the formation of branched flower and/or dendrite shape nano structures. Electroless plating of gold on silver metallic substrate in bath A - 2-Mercaptobenzothiazole produced star shaped gold nanostructures implying the effect of both bath composition and respective metallic substrate. Also the difference in reduction potential between gold and other metallic substrates influences the growth rate of gold nanostructures. When electroless plating conditions were maintained constant for all four substrates (Au, Ag, Cu and Ni), the resulting structures were observed to be unique for each metallic substrates. One of the major factors for such morphological variation in the gold nanostructure deposits might be due to the standard electrode potential of each metal substrate and the role of additives present in each bath composition.

Xia et al. have given a brief review over nucleation and growth within the context of metal nanocrystal synthesis, followed by a description of possible shapes that a metal nanocrystal might take under different conditions and also importance of reduction kinetics for shape control and seeded growth in the Au system [16]. Recent studies on the growth of single-crystalline dendritic gold nanostructures was reported and it was observed that in the growth process of gold dendrites, gold nuclei nanocrystals first forms on the substrate through a direct surface reaction and that the subsequent crystal growth preferentially takes place on the preformed gold crystals through a primary cell reaction, leading to the formation of final hyper-branched dendrites under non-equilibrium conditions [17]. One of the persuasive things involved in synthesis of metal nano crystals is that the chemical reactions often appears to be fairly simple but it is the nucleation and growth mechanisms behind the simple chemistry that is extremely complicated.

The present study provides a simple, cost-effective and efficient method of fabricating gold nanostructures of different shapes using electroless plating. Experimental study on the electroless deposition of gold nano structures for different concentration of additives and other important parameters like temperature, bath formulation procedure, nature of different metallic substrates, role of capping agents etc. are in progress. A successful attempt in achieving an economic and efficient outcome by using these fundamental concepts and existing knowledge could help us innovate much cost effective sensors for heavy metal ion detection in water. Further research may lead to the development of a robust sensor that find electrical, optical and diagnostic applications.

ACKNOWLEDGEMENTS

REFERENCES

[1] World Economic Forum - Future of Environment and Natural Resource Security, www.weforum.org.

[2] World Resources Institute – World's most water stressed countries, www.wri.org.

[3] R. Verma and B. D. Gupta, Food chemistry, **166,** 568 (2015).

[4] G. L. Turdean, International Journal of Electrochemistry, **2011**, 1 (2011).

[5] C. J. Murphy, T. K. Sau, J. Phys. Chem. B, **109**, 29 (2005).

[6] A. J. Mieszawska, W. J. M. Mulder, Z. A. Fayad, and D. P. Cormode Mol. Pharmaceutics, **831,** 10-3 (2013).

[7] P. R. Sajanlal, T. S. Sreeprasad, A. K. Samal, and T. Pradeep[*], Nano Reviews (2011).

[8] M. Sullivan and P. A. Kohl, J. Electrochem. Soc., **144**, 1686 (1997).

[9] X. P. Lei, G. Yu, Y. P. Zhu, Z. P. Zhang, X. M. He – International Journal of Surface Engineering and Coatings, **88,** (2010).

[10] M. J. Liew, S. Roy and K. Scott - Green Chemistry, Issue 4 (2003).

[11] W. J. Daukler, D. J. Resnick, W. A. Johnson and A. W. Yanof, Microelectron. Eng., **23**, 235 (1994).

[12] Y. Ohtani, A. Horiuchi, A. Yamaguchi, K. Oyaizu, M. Yuasa, J. Electrochem. Soc., **153**, C63 (2006).

[13] M. Kato, Y. Yazawa, and Y. Okinaka, AESF Annual Technical Conference Proceedings, 805 (1995).

[14] T. Osaka, A. Kodera, T. Misato, T. Homma, Y. Okinaka and O. Yoshioka, J. Electrochem. Soc., **144**, 3462 (2010).

[15] S. Dimitrijević, M. Rajčić-Vujasinović, V. Trujić Int. J. Electrochem. Sci., **8**, 6620 (2013).

[16] Y. Xia, Y. Xiong, B. Lim, Angew. Chem. Int. Ed. Engl., **48**, 60 (2009).

[17] Y. Qin, Y. Song, N. Sun, N. Zhao, M. Li and L. Qi, Chem. Mater., **20**, 3965 (2008).