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Nanoparticles of Coinage Metals as Nanoresonators and Their Applications in Analyte Sensing

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Abstract: **An overview of the preparation, characterization and applications of coinage metal nanoparticles have been presented in this article. These nanoparticles exhibit a varieties of colors upon their interaction with UV-VIS light and are also known as nanoresonators. The color variation is found to be a function of shape, size and concentration of nanoparticles. A characteristic surface Plasmon resonance band at a particular wavelength is observed for a particular type of nanoresonators in the UV-VIS region. The real time chemosensing/biosensing through an appropriate type of nanoresonators is a burgeoning area since last couple of decades. A few representative cases of chemosensing/bio-chemosensing through nanoresonators derived from copper, silver and gold have been presented over here.**

Index Terms: **Bio-sensing, Chemosensing, Colloids, Cysteine, Glutathione, Homocysteine, Nanochromophores, Nanoparticles, Nanoresonators Nanoscience, Nanotechnology, Sulfide, Surface Plasmon.**

I. Introduction

"*Where Nature finishes producing its own species, man begins, using natural things to create an infinity of species''*-Leonardo Da Vinci.

Although the day-to-day practices of nanoparticles (NPs) have been known since last 2000 years. Nevertheless, the systematic studies of the same could not be started until 1857 when *Michael Faraday* synthesized the ruby red gold nanoparticles in his own lab through a systematic chemical synthesis (*fig.1*). Now-a-days the nanoparticles have got a very wide range of applications from food packaging to textiles, cosmetics, medicines, optoelectronic devices, semiconductor devices, aerospace to catalysis. The very high surface area to volume ratio of nanoparticles is one of the responsible factor for their exotic properties. The modulation in colligative properties (*table I*) of a particular substance at its nanostage is marvellous and seeks the attention of scientists throughout the world.

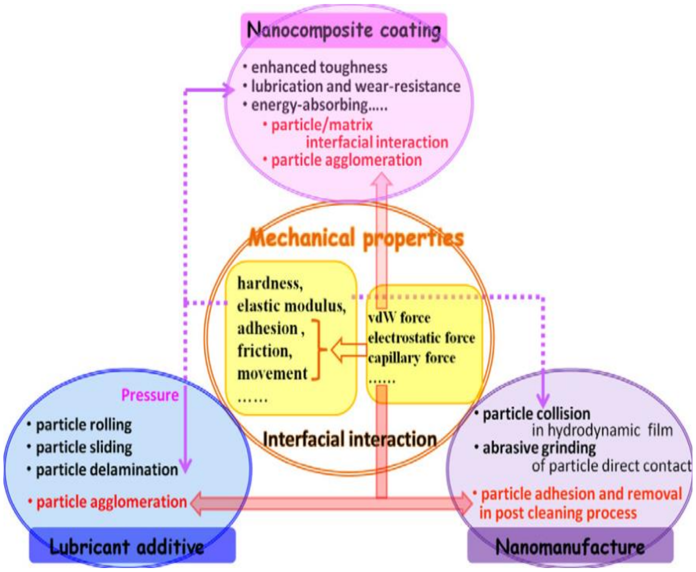
Fig. 1. (a) Michael faraday; (b) gold colloids (c) original samples synthesized by Faraday.

$$\mathbf{NaAuCl_4} \xrightarrow[\mathbf{CS_2}]{\mathbf{Phosphorus}} \mathbf{Gold\ Colloids}$$

It has also been observed that the mechanical properties of a material also get modified at its nanostage and make it more lucrative. The same has been represented below in scheme1.

Table 1. Property bulk *vs* nanoparticles.

Properties	Bulk Metal	Metal Nanoparticles
Melting Point	Ag= 961.8^{0}C; Au= 1064^{0}C	AgNPs(3.5nm)= 112^{0}C AuNPs(2.45nm)= 412^{0}C
Colour	Ag= White; Au= Yellow	AgNPs (smaller than 30nm)= light yellow AuNPS(~50nm)= ruby red
Surface Area	Ag coin(diameter=40nm) = -27.70cm^2	Ag coin divided into 1nm size= -11400m^2
Mechanical Strength	Ag= 251MPa; Au= 216MPa	AgNPs(13nm)= 3.12GPa AuNPs(22nm)= 1.72GPa



Scheme 1. Overview of mechanical properties

The size of nanoparticles ranges from 1-100nm (cf. average atomic size 1-2 A^0). For having a perception of the realm of nanoparticles in terms of their size an analogy can be used. If a hair is cut into 1 lakh pieces vertically then each and every piece corresponds to a nanoparticle. After the advent of most modern technologies like SEM, TEM and their high resolution versions people came to know that the nanoparticles can have 1D, 2D or 3D structures. The same can be represented in terms of chains, rings and clustures (*fig.2*).

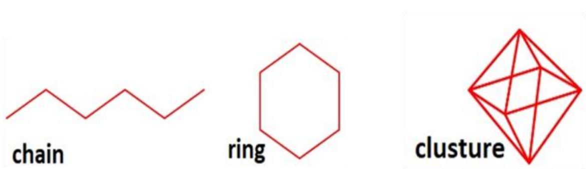


Fig. 2. structure of ring, chain and clusture

Clustures can have a variety of either simple polyhedron or the condensed ones. (*fig.3*)

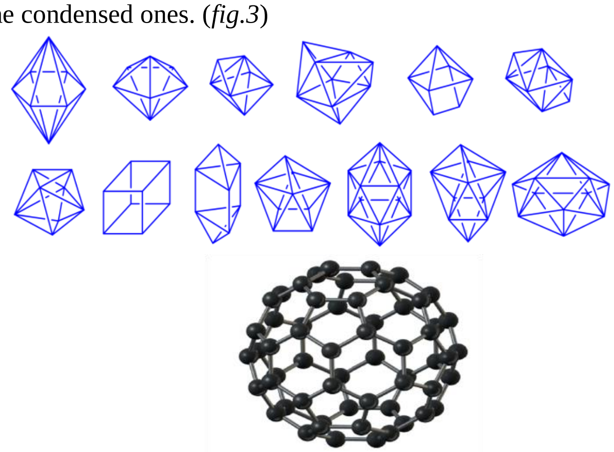


Fig .3. Simple and condensed polyhedral nanoclustures.

If anyone dimension of 2D /3D structures of a matter particle ranges from 1-100nm even then, such particles are considered under the definition of NPs. Following diagram provides a very good idea in nutshell about the comparative studies of a variety of natural /human creations with NPs (*fig.4*).

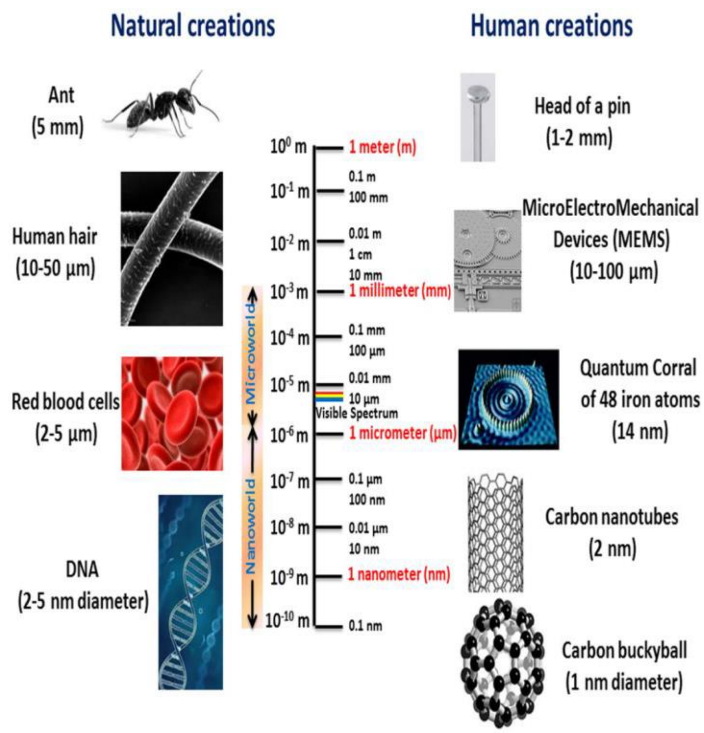


Fig. 4. Different creations by nature and humans at ultra-small level.

The royal society and royal academy of engineering have given a very convenient and modern definition of nanoscience and nanotechnology- "*Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where the properties differ significantly from those at a larger scale*"; likewise, "*Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale*". The tunable physicochemical characteristics such as melting point, wettability, electrical and thermal conductivity, catalytic activity, light absorption and scattering resulting in enhanced performance over their bulk counterparts have lured the scientific community to do researches in this field. The interaction of NPs particularly of coinage metals viz. Cu, Ag and Au with UV-VIS light produces varieties of mesmerizing colors which can be tuned with their shape, size and interparticle distances (concentration). That's why, these metal NPs are also termed as nanoresonators due to their ability to undergo resonance with the UV-VIS light of a particular frequency.

II. History: The Journey of Nanoparticles

The practices in the field of nanoscience dates back since last 2000 years in the eastern as well as western worlds. In India the nanoparticles of iron, copper, silver and gold were known in the field of ayurveda as therapeutic agents in the form of their bhasma's (louh, tamra, rajat and swarna). The gold bhasma along with honey and cow ghee was in prevalent use for curing diabetes mellitus, bronchial asthma, rheumatoid arthritis, and nervous disorder . On the other hand a glimpse of nanoscience can also be seen in roman history in the form of Ag NPs and Au NPS as the coloring agents for the glasses of windows and domes of churches. "Lycurgus cup" is the best example of this, which is also known as *cage cups* or *diatreta* and shows "Dichroic effect" and appeares pea green in reflected light but wine red in transmitted light (*fig.5*). At that time no one was aware about the reason behind this.

(i)

(ii)

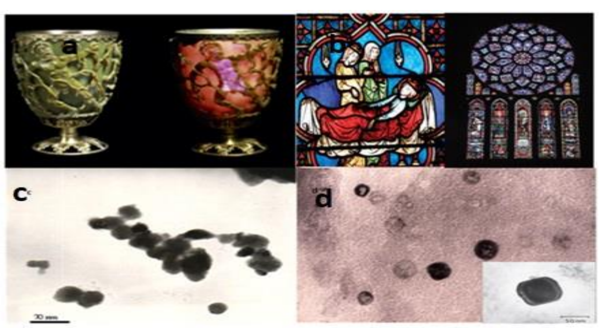


Fig. 5. (i) Ash of metals (a) iron (b) copper (c) silver (d) gold (swarn bhasma) (ii) (a) effect of light(reflected /transmitted light) on Lycurgus cup (b) colored glass windows of churches shows different color (c) TEM image of swarna bhasma (d) TEM image of a sample of glass of Lycurgus cup (particle size approx 50nm)

A glimpse of historical development in the field of nanoparticles at different times can be had from *Table II* .

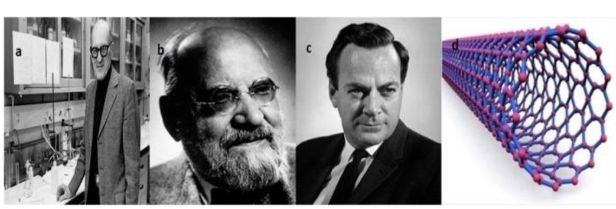


Fig. 6. (a) turkevich; (b) Gustav Mie; (c) R. Feynman; (d) carbon nanotube

Table 2. Schemetic development in field of nanoscience

Year	Discoveries	People
2000 years ago	Swarna Bhasma	Indian Ayurveda
290-325AD	Lycurgus cup	Alexandria or Rome
1857	Gold colloids synthesis	Michael Faraday
1902	Surface Plasmon Resonance(SPR)	R.W.Wood
1908	Mathematical correlation between size of nanoparticles and their optical behaviour	Gustav Mie
1931	Transmission Electron Microscope(TEM)	M. Knoll and E. Ruska
1937	Scanning Electron Microscope(SEM)	M.Von Ardenne
1959	Lecture on ‘‘ There's plenty of room at the bottom''	Richard P. Feynman
1974	Concept of Nanotechnology	N.Taniguchi
1976	Carbon nanofiber	M.Endo
1982	Scanning tunneling microscope (STM)	G.Binnig and H.Rohrer
1986	Atomic Force Microscope(AFM)	G.Binnig
1991	Carbon nanotubes	S. Iijima
2017	Cryo- transmission electron microscopy for understanding functioning of ribosomes	J.Dubochat, J.Frank and R.Henderson

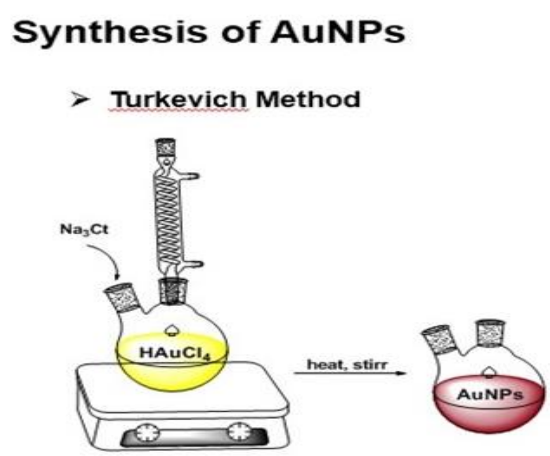


Fig.6 (e) turkevich's synthesis of AuNPs .

III. Nanoresonators in Nature

A number of live forms particularly from the animal kingdom have got beautiful colors over their body parts. e.g. peacock, a few other birds and flies (*fig.7*).

Fig.7. beautiful effects(structural and functional) because of nanoparticles observed in (a) peacock (b) butterfly (c) chameleon (d) surkhab bird

The chameleon exhibits color adjustment of its skin as per its surrounding environment which is a kind of safety measures from their enemies. This instant color change is supposed to be due to guanine nanocrystals embedded beneath their skin. As per signals through neurotransmitter the orientation of nanocrystals change which further leads to change in the frequency of reflected light which finally leads to change in color of their skin. Infact the various colors shown in fig.7 are all due to various kinds of nanocrystals. These exhibit variation in their ability to absorb visible light depending upon their shape size and interparticle distances. The same are also known as structural colors and such type of nanoparticles are better referred as nanochromophores.

IV. Interaction of Nanoparticles with Light; Resonance at Nanoscale

Nanoparticles of noble metals particularly of coinage metals have been found to exhibit varieties of colors different than the colors in their bulk state (*fig.8*).

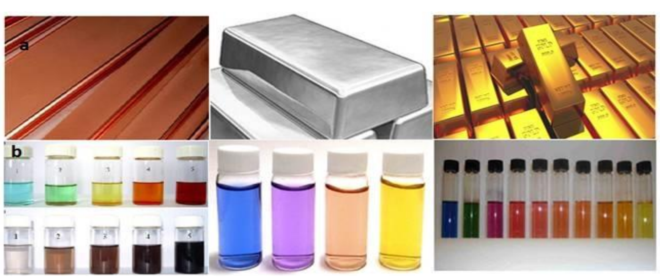


Fig. 8. Coinage metal (Cu, Ag & Au) in their bulk state (a) and at nanoscale level (b) showing different colors

The variation of these colors depends upon the shape, size and interparticle distance of nanoparticles that's why they are also refered as structural colors (*fig.9*). The refractive index as well as dielectric constant of the medium also affect the colour of these NPs.

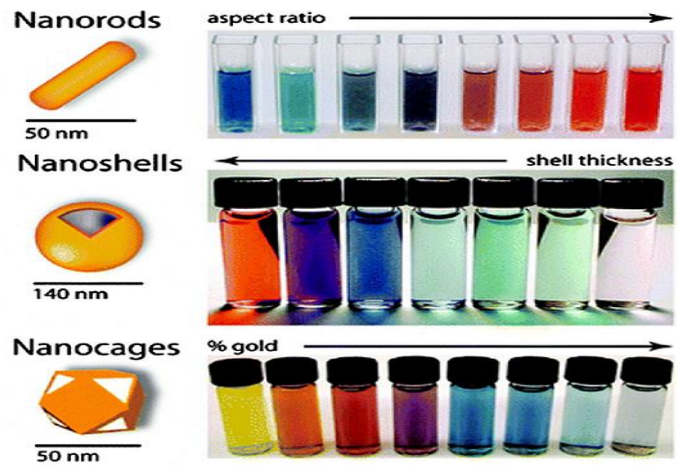


Fig. 9. Variation in colour of nanoparticle w.r.t. shape, size and interparticle distances.

The fundamental reason behind the origin of above colors is surface Plasmon resonance(SPR) of metal nanoparticles with light and constitutes a discipline known as 'plasmonics'. The very first theoretical account of plasmonic effect was presented by *A. Sommerfeld* in 1899 while the experimental studies were performed by R. Wood in 1902. A few other physicists *viz J.C. Maxewell Garnett, Gustav Mie* and *G. Beirtrage* developed a full theory of scattering of light by nanostructures. The SPR bands of various coinage metal nanoparticle have been shown below (*fig.10*)

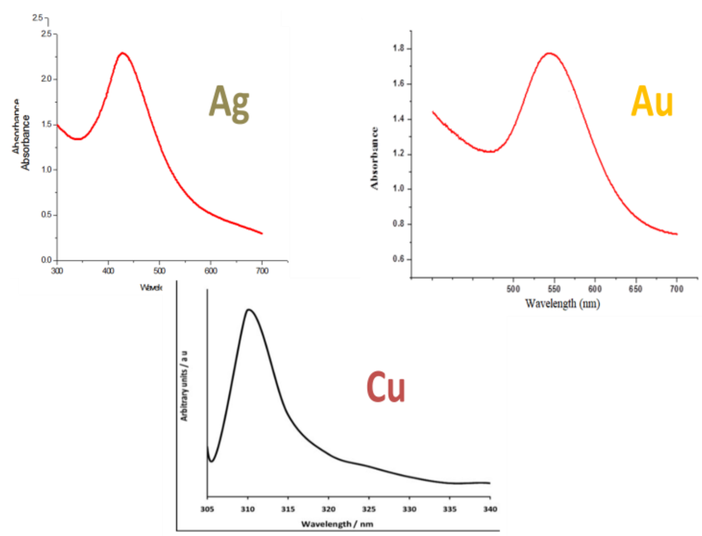


Fig.10. Surface Plasmon band of coinage metals (silver, gold and copper)

During this interaction the scattering and absorption of incident light take place. The extent of these two are quite interdependent and strongly depends on size of MNPs (metal nanoparticles). If the particle size is smaller (<15nm) then absorption dominates over scattering and vice versa. The free electrons in noble metals are known as Plasmon. This Plasmon is nothing but a quantum of plasma oscillation. The energy of these oscillations can be given through following equation

$$E_p = \hbar\sqrt{\frac{ne^2}{m\varepsilon_o}} = \hbar\omega_p$$

e and m =electron charge and mass, $n = electron\ density$, $\mathcal{E}o$ = permittivity of free space ω_p = frequency of oscillation

When these NPs are irradiated the surface Plasmon of these metals get coupled with electromagnetic field of incident radiation and a situation of resonance is established. This is also known as Plasmon resonance. The dependence of energy of surface Plasmon resonance on shape and size of the NPs can be understood through following diagrams. (*fig.11*)

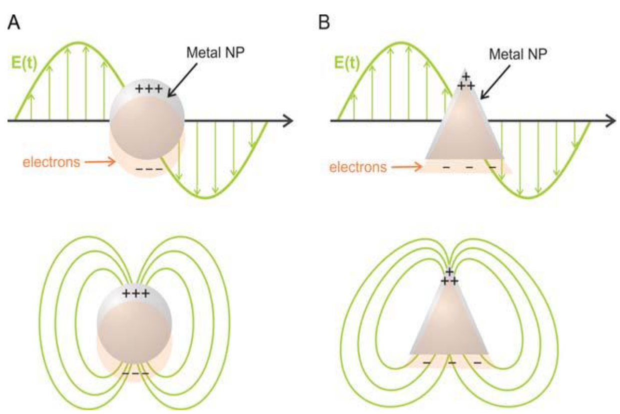


Fig. 11. Schematic representation of the SPR of NPs with the shape of a sphere (A) and a triangular prism (B).

The oscillation of these nanoresonators (nanoparticles) can be modulated in a specific way by a specific analyte under the given set of conditions. By this way the same can be used as the chemosensors for various kinds of analytes. The chemical literature is full of such reports. Such nanoresonators for the chemosensing/biosensing purposes can be synthesized in the laboratory. The wet chemical method is one of the most widely used method for this purpose and is a kind of bottom-up approach. In this method a particular concentration of a suitable metal salt is dissolved in a specified amount of milli-Q water. A suitable chemical reducing and capping agent are added in this metal salt solution with constant stirring at a specified temperature and pressure. The reaction medium is further made alkaline by the addition of a suitable alkali solution of a particular concentration. The preparation of nanoparticle is indicated by the color change of the reaction medium which is further confirmed by various spectroscopic techniques like UV-VIS, IR, RAMAN etc. beside SEM, TEM and EDAX/EDS studies. The SEM, TEM studies indicate the level and type of crystallinity of the nanoparticles. This entire process can be depicted schematically as follows (*fig.11*)

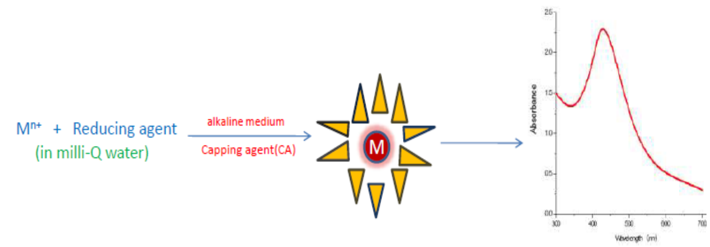
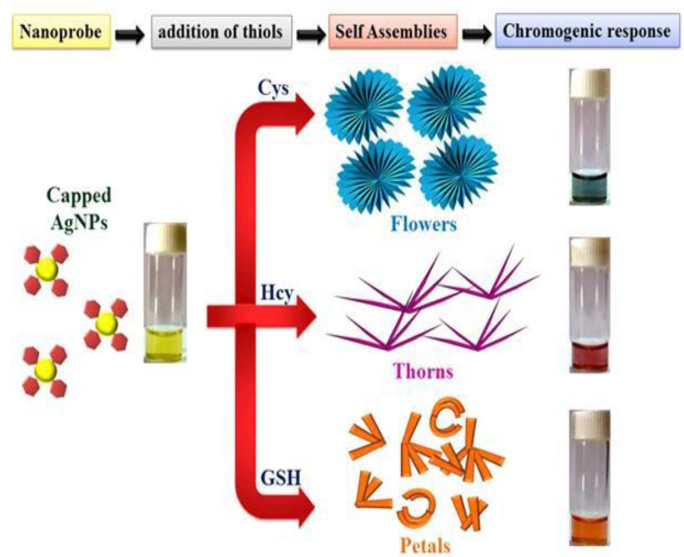


Fig. 11. Schematic plan of synthesis and characterization (via UV-VIS) of nanoparticles.

A wide variety of reducing and a capping agents under variable experimental set of conditions have been used for the synthesis of NPs of coinage metals. Our own research group has successfully demonstrated the preparation and uses of silver and gold nanoresonators through wet chemical method for the smart sensing of a number important analytes like sulfide and a few biothiols viz. cysteine, homo-cysteine and glutathione.



(I.Sanskriti and K. K. Upadhyay, New J. Chem., 2017, 41, 4316-4321)

Wel-Lung Tseng et al synthesized Tween-20 stabilized gold nanoparticle which gave colorimetric sensing of Ag (I) and Hg (II) ions. The Gold Nanoparticles synthesized *by Huan-Tsung Chang et al* were used as fluorogenic as well as Chromogenic Sensing of mercury (II) Ions with LOD of 5.0 nM. *Daoben Zhu et al.* prepared Gold Nanoparticle-Based Fluorogenic and Chromogenic nanosensors for the real time sensing of Copper (II) Ions (*fig.12*).

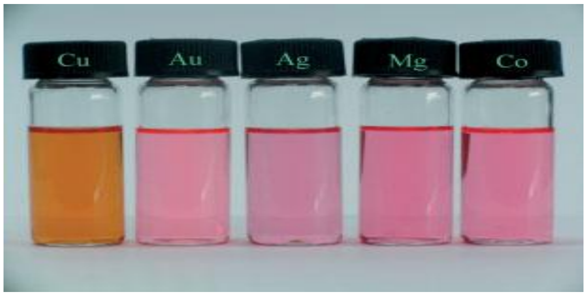


Fig. 12. Chromogenic sensing of Cu2+ by gold nanoparticles prepared by Daoben Zhu Fig. 12.

The research group of *Kemin Wang* prepared a Poly (thymine)-Templated Copper Nanoparticles and exploited the same as a fluorescent Indicator for Hydrogen Peroxide and Oxidase-Based Biosensing, with a minimum detectable concentration of anlytes as 0.55 μM. A very efficient colorimetric nanosensor for mercury ion was presented by Razium A. Soomro et al. The same was composed of copper nanoparticpes protected over L-cysteine. *K. K. Upadhyay* et al. reported Silver nanoparticles templated over an azo phenol as a highly efficient and selective optical probe for the sensing of sulphide via dendrimer formation in aqueous medium. A yet another silver nanoprobe functionalized by 4,4-bipyridine was reported by *Haibing Li et al.* for the efficient colorimetric sensing of tryptophan. An excellent one-step synthesis of silver nanoparticles stabilized by dopamine was reported by *Yaqi Cai et al.* for the efficient visual detection of melamine in raw milk upto its lowest level of 0.01ppm (fig.13).

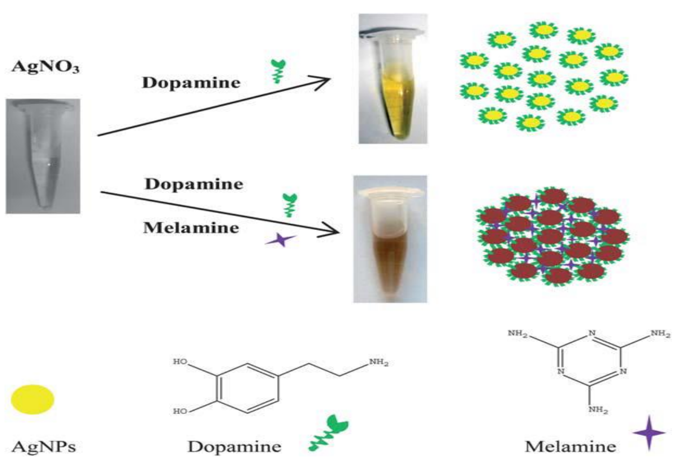


Fig. 13. Dopamine capped colorimetric detection of melamine

CONCLUSION

Thus, the nanoparticles of coinage metals i.e. Cu, Ag, Au have come up as a very potent candidates for the real time chromogenic/fluorogenic sensing of a variety of analytes including those of biological importance also. Their total water compatibility provides them an edge over molecular chemosensors which normally exhibit poor water solubility. As has been discussed above that the resonating behavior of these nanoparticles is highly dependent on their shape, size and concentration, hence the same can produce a variety of mesmerizing colors. These nanoresonators have a bright future as a colorant also and these can be a good substitute of dyes and pigments of organic nature.

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