

“Semiconductor Nanoparticles Synthesis in Solution”

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Date of Submission: 15-07-2019

Date of acceptance: 31-07-2019

I. Introduction

Nano Particles

In nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties. It is further classified according to size : In terms of diameter, fine particles cover a range between 100 and 2500 nanometers, while ultra fine particles, on the other hand, are sized between 1 and 100 nanometers. Similarly to ultra fine particles, **nanoparticles** are sized between 1 and 100 nanometers, though the size limitation can be restricted to two dimensions. Nanoparticles may or may not exhibit size-related properties that differ significantly from those served in fine particles or bulk materials.

Nano clusters have at least one dimension between 1 and 10 nanometers and a narrow size distribution. Nanopowders are agglomerates of ultra fine particles, nanoparticles, or nanoclusters. Nanometer sized single crystals, or single-domain ultra fine particles, are often referred to as nanocrystals. Nanoparticle research is currently an area of intense scientific research, due to a wide variety of potential applications in biomedical, optical, and electronic fields. The National Nanotechnology Initiative has led to generous public funding for nano particle research in the United States.

Although generally nanoparticles are considered an invention of modern science, they actually have a very long history. Specifically, nano particles were used by artisans as far back as the 9th century in Mesopotamia for generating a glittering effect on the surface of pots.

Even these days pottery from the Middle Ages and Renaissance often retain a distinct gold or copper colored metallic glitter. This so called lustre is caused by a metallic film that was applied to the transparent surface of a glazing. The lustre can still be visible if the film has resisted atmospheric oxidation and other weathering.

The lustre originates within the film itself, which contains silver and copper nanoparticles, dispersed homogeneously in the glassy matrix of the ceramic glaze. These nanoparticles were created by the artisans by adding copper and silver salts and oxides together with vinegar, ochre, and clay, on the surface of previously-glazed pottery. The object was then placed to a kiln and heated to about 600°C in a reducing atmosphere.

In the heat the glaze would soften, causing the copper and silver ions to migrate into the outer layers of the glaze. There the reducing atmosphere reduced the ions back to metals, which then came together forming the nano particles that give the colour and optical effects.

Lustre technique shows that craftsmen had a rather sophisticated empirical knowledge of materials. The technique originates in the Islamic world. As Muslims were not allowed to use gold in artistic representations, They had to find a way to create a similar effect without using real gold. The solution they found was using lustre.

Michael Faraday provided the first description, in scientific terms, of the optical properties of nanometer-scale metals in his classic 1857 paper “Experimental relations of gold (and other metals) to light.”

Much of the modern day studies of these objects have been conducted at the ESRF laboratory. Several techniques were used to characterise the chemical and physical properties of these lustre, such as Rutherford Backscattering Spectrometry (RBS), optical absorption in the visible-ultraviolet region, electron microscopy (TEM and SEM).

II. Results , Discussion & Conclusion

The optical images of the transparent, agarosestabilized metal nanoparticles gels are shown in it shows a light brown colour for Pt and Pd, turmeric yellow for Ag, bright red for Au and a wine red colour for Cu nanoparticles stabilized by agarose polymer. Prolonged drying for 48 h at room temperature allows these gels to become transparent composite films with a slight reduction in the intensity of the original colours.

In the case of agarose-copper composite gel, the wine red colour slowly transformed to pale green on drying due to partial oxidation of copper in air. The UV-Vis spectra of ‘the dried films show plasmonic bands in the visible region at 420, 520 and 585 nm respectively for Ag, Au and Cu nanoparticles loaded composites, On

the other hand, the Pt and Pd nano particles composite films do not show any sharp plasmon band and the absorption is spread over the entire visible region.¹¹

The fine dispersion of metal nano particles throughout the agarose matrix is evident from the transmission electron microscopic (TEM) images of the composite films in The agarose matrix that appears in light contrast in comparison to the electron dense metal nano particles is highly porous in nature and the sizes of the macropores are in the range of 50 to 200 nm. Au and Ag nanoparticles of sizes less than 10 nm are well dispersed inside the agarose matrix. Occasionally, few silver nano particles of size around 30 nm are seen in the larger pores of agarose network. In the case of copper, the particles size fall far below 5 nm and are evenly distributed in the agarose network seen from the uniform dark contrast in the TEM image. These findings suggest that the presence of functional groups such as hydroxyl and ether linkages in the agarose network

Optical images of agarose-metal nanoparticles composites-(a) (i) Pd,

(ii) Pt,

(iii) Ag,

(iv) Au and

(v) Cu Nanoparticles in agarose matrix and

(b) Corresponding UV-Vis absorption spectra.

TEM images of

(a) Au,

(b) Ag,

(c) Pt, and

(d) Cu nanoparticles in agarose matrix.

Insets in images (a—c) show the histogram of particle size distribution of corresponding nanoparticles, the inset in image (d) shows the higher magnification image of Cu nanoparticles. effectively help in passivating the surface of nanoparticles. Interestingly, reduction of Ag and Au ions using glucose within the agarose medium gives bright yellow and violet coloured Ag-, and Auagarose composites. (figure 3a). The corresponding plasmon bands in the UV-Vis spectra shifted to longer wavelengths (nearly 30 nm, figure 3b) compared to the composites prepared using sodium borohydride as the reducing agent. This shift in the plasmon band for higher wavelength is associated with the larger particle sizes obtained by the slow diffusion of reducing agent, glucose, compared to NaBH₄ inside the agarose matrix.

The gel forming ability and the oxygen-based functional groups of agarose polymer are not only used to stabilize metal nanoparticles but also the semi conducting metal sulphide nanoparticles. The optical image of the semi conducting PbS, CdS and ZnS nanoparticles encapsulated in agarose matrix is shown in figure 3c. The CdS and PdS nanoparticles impart yellow and dark-brown colours respectively to the agarose matrix whereas, the ZnS nanoparticle impart no colour to the gel. The transparent nature of the composite films confirms the presence of metal sulphide particles in the nanosize regime. The UV-Vis absorption spectra of the agarose-semiconductor nanoparticles composites are in The CdS-agarose composite film obtained after drying the gel in air at 30°C shows a characteristic absorption band edge at around 450 nm. ¹² The PbS-agarose composite film also shows a broad absorption all through the visible region in addition to a strong absorption below 380 nm. On the other hand, ZnS-agarose composite did not show any abSynthesis of agarose-metal/semiconductor nanoparticles

(a) Optical images of

(i) Agarose gel,

(ii) Au nanoparticles in agarose, and

(iii) Ag nanoparticles in agarose and

(b) Corresponding UV-Vis absorption spectra.

(c) Optical images of

(i) CdS,

(ii) PbS, and

(iii) ZnS nanoparticles in agarose matix and

(d) Corresponding UVVis absorption spectra. Sorption in the visible region but only in the UV region below 320 nm. The photoluminescence spectrum of the CdS-agarose film (CdS particle size around 2 nm, TEM image is not shown) excited at 350 to 400 nm shows a broad yellow-orange emission with the peak maximum at 580 nm associated with the CdS nanoparticles.

(figure S2 in the Supporting Information).

In case of ZnS agarose film, excitation at 300 nm resulted in blue emission at 435 rim (figure S3 in the Supporting Information). The transparent nature of the agarose-metal sulphide composite films coupled with their strong absorption in the UV and visible region would find application in UV and colour filters.

The antibacterial activity of silver and copper nanoparticles in the agarose matrix was tested on the bacteria *E. coli*. The antibacterial activity of silver nanoparticles is attributed to the increased chemical reactivity owing to their higher surface area to volume ratio.

13. The changes in the local electronic structure on the surfaces of the smaller sized particles leads to the enhancement of their chemical reactivity leading to bactericidal effect.

14. Various mechanisms, through which silver nanoparticles kill bacteria, have been proposed. They are known to destabilize the plasma membrane potential leading to the depletion in the levels of intracellular ATP bringing about cell death. They are also known to act through the formation of complexes with biomolecules containing sulfur, oxygen and nitrogen, such as thiols, carboxylates, amides, imidazoles, indoles and hydroxylates in proteins.

15. Silver nanoparticles are also shown to display affinity towards phosphorous containing compounds. Peroxide and free radical generation by silver nanoparticles is yet another mode by which they kill bacteria.

16. The excellent property of conformational entropy displayed by silver nanoparticles in polyvalent binding makes it easier for them to attach to flexible polymeric chains.

17. These observations assume significance in the light of the increasing antibiotic resistance displayed by bacteria. Similarly, copper ions, either alone or in copper complexes, are known as antimicrobial agents.

18-21 However, there are only a few reports on the antibacterial activity of copper nanoparticles.

22-25 This study utilizes the *E. coli* strain DH5 α for checking the antibacterial action of silver and copper nanoparticles dispersed in the porous agarose matrix. *E. coli* is a gram negative, facultative anaerobic, non-sporulating, motile, rod shaped bacterium commonly found in the lower intestine of warmblooded animals. The antibacterial potency of silver and copper nanoparticles at two different concentrations stabilized by LB-agarose. Antibacterial activity assay for silver and copper nanoparticles. The nanoparticles were synthesized in LB agarose and the bacteria were plated on them. Note that at higher concentration of Ag and Cu nanoparticles the colour of the gel gets little darker.

(a) Upper left, agarose gel and bacteria; Upper middle, agarose gel with NaBH₄ and bacteria; Upper right, agarose gel with silver nitrate and bacteria; Bottom left, agarose gel without bacterial inoculation; Bottom middle, agarose gel containing low concentration of Ag nanoparticles (about 5 μ g of Ag per gram of gel) and bacteria; Bottom right, agarose gel containing high concentration of silver nanoparticles (about 10 μ g of Ag per gram of gel) and bacteria.

(b) Upper left, agarose gel and bacteria; Upper middle, agarose gel with hydrazine hydrate and bacteria; Upper right, agarose gel with copper sulphate and bacteria; Bottom left, agarose gel without bacterial inoculation; Bottom middle, agarose gel with low concentration of Cu nanoparticles (about 3 μ g of Cu per gram of gel) and bacteria; Bottom right, agarose gel with high concentration of Cu nanoparticles (about 6 μ g of Cu per gram of gel) and bacteria.

Both silver and copper nanoparticles showed effective inhibition as shown in the figures 4 a and b. Two types of bacterial inhibition, viz. bacteriocidal or bacteriostatic, are known to be caused by the application of nanoparticles on bacterial cultures. In bacteriocidal effect, the nanoparticles kill the bacteria and hence, prevent their growth in any fresh medium whereas, in bacteriostatic effect, they keep the bacteria dormant, giving room for their resuscitation in a suitable medium. In our case, both Ag and Cu nanoparticles show complete bacteriocidal effect as seen when the surface of the LB agar plate was scraped and restreaked onto a fresh plate, without nanoparticles, after three days.

The absence of any colony growth on restreaking confirms the bacteriocidal effect of the Ag and Cu nanoparticles. The LB/agarose stabilized silver nanoparticles prepared with lower concentration of silver (about 5 μ g of Ag per gram of composite gel) showed nearly 50% inhibition of bacterial growth while doubling the concentration (about 10 μ g of Ag per gram of composite gel) displayed complete inhibition (figure 4a). In the case of copper, complete inhibition was observed even at lower concentration (at about 3 μ g of Cu per gram of composite gel) indicating the superior bacteriocidal activity of copper nanoparticles over silver nanoparticles (figure 4b). This is particularly significant when we compare the concentration of Ag nanoparticles used in other studies. For example, Kumar et al²⁶ used nearly 3000 μ g of Ag (in the form of nanoparticles) per gram of alkyd paint and 4000 μ g of Au (in the form of nanoparticles) per ml of vegetable oil for antimicrobial coatings. Similarly, Morones et al¹³ reported silver nanoparticles solution containing 75 μ g of Ag/ml showing good antimicrobial activity.

nm are known to have effective bactericidal activity^{13,27-29} contributed by Ag⁺ and Ag⁰. The agarose matrix in our study plays a dual role for the exhibition of high antibacterial activity of nanoparticles even at very low metal concentration. It not only helps to stabilize the Ag and Cu nanoparticles of very small sizes by their functional OH groups but also facilitate the full exposure of these nanoparticles to the microorganism due to their large porous network.

III. Conclusions

In conclusion, transparent agarose-metal/semiconducting nanoparticle composite films were made. Synthesis of agarose-metal/semiconductor nanoparticles. Field-emission scanning electron microscopic (FESEM) images of (a) Au- and

(b) Ag-carbon composites after carbonization.

TEM images of

(c) Au- and

(d) Ag-carbon composites.

(a-b) Insets show the particle size histogram of corresponding nanoparticles inside the carbon matrix, by a simple route without compromising the optical properties of the nanoparticles. The high level antimicrobial activity of the Ag and Cu nanoparticles stabilized in the porous agarose matrix can be utilized in food packaging, sanitation and fabrics. More importantly, the agarose-metal nanoparticles films can be readily converted into carbon-metal nanoparticles composites by carbonizing the films in nitrogen environment at 400°C for 30 min. The obtained composites show fine distribution of metal nanoparticles (average particles size of 9 nm and 30 nm. for Au and Ag respectively, on carbon matrix whose applications in catalysis are well known.³⁰

Chemical Aerosol Flow Synthesis of Semi conductor Nanoparticles

IOSR Journal of Applied Chemistry (IOSR-JAC) is UGC approved Journal with Sl. No. 4031, Journal no. 44190.

Anuj Sharma. “Semiconductor Nanoparticles Synthesis In Solution”. IOSR Journal of Applied Chemistry (IOSR-JAC) 12.7 (2019): 84-87.