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Synthesis of 2-aminocyclopent-1-ene-1-carbodithioic acid (ACA) Capped Silver nanoparticles, Characterisation and Fluorescence application

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ABSTRACT

The present work deals with the formation, morphology and photophysical activity of the 2-aminocyclopent-1-ene-1-carbodithioic acid (ACA) Capped Silver nanoparticles via chemical reduction method. The method utilizes a simple chemical reaction of silver idodide and sodium borohydride. The advantages of this method are ease of preparation, convenience in use and especially, that the obtained silver nano particles are uniform in their shapes and sizes. This is important for fluorescence & bio-evolution measurements. Furthermore, UV-visible (UV-vis) spectroscopy is employed to monitor the formation process of the nano particles and to determine the optimum conditions for the preparation of stable and highly fluorescence-active silver colloids. Specifically, we observed changes in the shapes of the silver nano particles during the formation. This may be helpful in understanding the growth of the nano particles and creates a new dimension in controlling the shapes of the nano particles.SEM, TEM and XRD studies are carried out. The suitability of ACA capped Ag-NPs as Biomarkers is also Tested by Fluorescence study.

Key words – Biomarkers, Capped Silver Nanoparticles, Chemical Reduction, Fluorescence.

I. INTRODUCTION

Recently, fluorescent nanoparticles, have attracted much attention for a variety of purposes and applications in biology and medicine, for example, in immuno-labeling,[1] as cell markers,[2] in cell motility assays,[3] in biological assembly,[4] and especially in optical imaging agents,[5] due to their photostability and other excellent optical properties. Due to the urgent need of environmentally-friendly fluorescent nanoparticles, the emerging carbon dots (CDs) appear to be a promising alternative to semiconductor QDs in many applications such as bioimaging, disease detection, and drug delivery [6] because of their superiority in chemical inertness, biocompatibility, low toxicity, cheaper cost and promising upconversion property.[7]

However, the fluorescent intensity of Carbon Dots is relatively low in most reports,[8] but metal (such as gold or silver) has an enhanced effect on the fluorophore, as known as metal-enhanced fluorescence (MEF).[9] It is well established that the interactions of fluorophores with silver nano particles results in an increased photostability, fluorescence enhancement, and a decreased lifetime due to increased rates of system radioactive decay.[10] The fluorescence enhancement noted in these studies can stem from a mechanism of surface Plasmon resonance.[11] Excellent overlap of the CDs absorption/emission spectrum with the scattering spectrum of the silver surface is required for effective surface plasmon resonance, while CDs show a broad absorption and emission spectrum, which provides a good overlap with the silver scattering spectrum.[12]

The spontaneous emission of light by molecules and atoms at nano structured metallic surfaces is remarkably modified due to a complex interplay of enhancing and quenching physicochemical processes. Fluorescence enhancement can be promoted by surface plasmons excited in metal and by a modified density of photon states in a nano structured surface,[13] while quenching processes include chemical bonding and non radiative energy transfer from the luminescent species to the metal. Importantly, the degree of metal-fluorophore interactions strongly depends on the distance between the fluorophore and the metal surface.

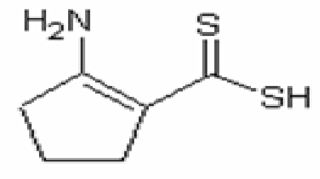
In the present study, ACA Capped Ag-NPs are prepared by a simple, direct chemical Reduction Method and is Tested for its suitability as Biomarker by studying Florescence Emission Spectra of the prepared Ag-NPs.

II. Materials & Methods

2.1 Chemicals & Instruments Used

All the reagents used were of AR grade. Silver nitrate was obtained from National Refinery Pvt. Ltd, and a 0.1 M aqueous solution was used as stock solution. Sodium borohydroxide was obtained from

Merck, India. Organic-free water was used throughout the experiment.

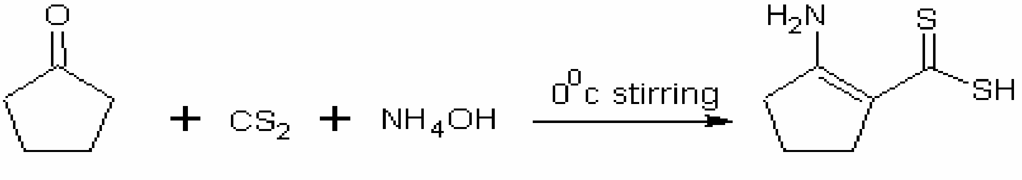


2-aminocyclopent-1-ene-1-carbodithioic acid (ACA)

The UV-visible spectra were recorded on a Schimadzu UV-vis spectrophotometer, and the solutions were taken in a 1 cm well-stopper quartz cuvette. Fourier transform infrared (FTIR) spectral characteristics of the samples were collected on a Schimadzu FTIR spectrometer with the samples as KBr pellets. The FTIR spectrum was recorded over 45 scans of each sample, and the background spectrum was automatically subtracted. The formation of single-phase compound was checked by X-ray diffraction (XRD) technique. The XRD pattern was taken with X-ray diffractometer (XPERT-PRO) at room temperature, using CuK$_\alpha$ radiation λ=1.5406 A$^\circ$ over a wide range of Bragg angles ($30^0 \leq 2\theta \leq 85^0$). SEM micrograph of ACA capped Ag-NP was obtained at 20 K data was obtained on a F20 Tecnai High Resolution microscope (Philips, Netherlands). For SEM analysis, the specimen was suspended in distilled water, dispersed ultrasonically to separate individual particles, and one or two drop of the suspension deposited onto holey-carbon coated copper grids and dried under Infrared lamp. Fluorescence spectra were measured on a Schimadzu spectrofluorometer. The optical path was 1 cm and spectra were collected at a resolution of five data points per nanometer. When recording fluorescence spectra the total absorption in no case exceeded 0.06, making the necessary correction for the inner filter effect small.

2.2 Synthesis of 2-aminocyclopent-1-ene-1-carbodithioic acid (ACA):

Cyclopentanone (25.02g) was mixed with 27.5 ml carbon disulfide in 100 ml concentrated ammonium hydroxide (28% solution) in a 250-ml flask. The mixture was stirred at 0^0C in an ice bath for 6 h (scheme-1). A yellow precipitate gradually falls out of the solution. The crude product was recrystalized from ethanol. That was ammonium salt from the dithio acid and was fairly unstable. Thus, the salt was collected by suction filtration and was immediately dissolved in about 200 ml of water. Then, with vigorous stirring, 2M HCl was added until the pH reached 4-5. A yellow precipitate would be formed. That was the free dithioacid. The free acid was collected by suction filtration and was washed several times with water and was dried. This procedure was done according to the earlier recommended report [14]. The crystals were recrystalized from ethanol. The IR spectra showed (KBr disk method) 3450, 1618, 1605, 1470, 1450, 1425.The NMR spectra showed (in DMSO) δ 10.7(m, NH), 9.0(s, SH), 3.40(t, C-1 H), 2.95(t, C-5 H2), 2.72 (t, C-3 H2), 1.85(m, C-4 H2) which are in agreement with the earlier reported procedure.



2.3 Synthesis of ACA Capped Silver Nano particle Assembly:

A total of 2.5 mL of 10^{-2} M $AgNO_3$ was added to 75 mL of triply distilled organic-free water. A total of 5 mL of 10^{-2} M 2-aminocyclopent-1-ene-1-carbodithioic acid (dissolved in hot water) was added as stabilizer to the solution with stirring. After 10 min of mixing, 2.5 mL of 10^{-2} M Sodium Iodide (NaI) was dropped into the solution slowly, yielding a green yellow AgI colloid. A total of 20 mg of $NaBH_4$ was added to the AgI colloidal solution, and the reaction mixture was continually stirred for about 20 min. The silver colloid was finally obtained. During the whole reaction, the color of the colloidal solution changed from yellow to brown at the beginning, then finally to black.

2.4 Results and discussion

Evolution and Characterization of Silver Nano particle Aggregates:

UV–vis spectroscopy Study:

The aggregates of silver nano particles have been synthesized using silver nitrate as the precursor salt and ACA as the capping agent. The successive changes of the absorption spectra of synthesized silver nano particles aggregates are shown in Figure 1. After the addition of $AgNO_3$ to the sodium iodide solution, the color of the solution changes from colorless to light yellow indicates the nucleation of the silver particles at their infancy. The UV absorption measurements of the synthesized nano particles were further studied by dissolving in solvent DMSO.

"Fig" 1 shows the UV-vis spectra of silver colloids obtained. The surface Plasmon resonance

(SPR) band is broad indicating poly-dispersed nano particles. A smooth and narrow absorption, a band at 421 nm is observed in DMSO solvent of ACA capped Ag-NP by above procedure, whereas 390 nm is observed for ACA in DMSO which clearly indicates the formation of silver colloids. UV-visible spectroscopy is one of the most widely used techniques for structural characterization of silver nano particles. The optical absorption spectra of metal nano particles are dominated by surface plasmon resonances (SPR), which shift to longer wavelengths with increasing particle size. The position and shape of plasmon absorption of silver nano clusters are strongly dependent on the particle size, dielectric medium, and surface-adsorbed species. The surface plasmon absorption of silver nano particles have the short wavelength band in the visible region around 409 nm is due to the transverse electronic oscillation.

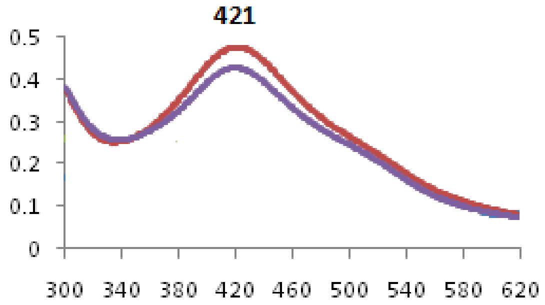


Fig. 1. UV–vis absorbance spectra of 2-aminocyclopent-1-ene-1-carbodithioic acid capped AgNP in DMSO.

2.5 Scanning electron microscopy study:

The SEM images obtained for colloid is shown in “Fig.” 2. It is clear from the SEM images in Fig. 2, that the particles are nearly crystalline spherical particles respectively.

The Scherrer rings, characteristic of fcc silver is clearly observed, showing that the structure seen in the SEM image are nano crystalline in nature. It is observed that the silver nano particles are scattered over the surface and no aggregates are noticed under SEM. The difference in size is possibly due to the fact that the nano particles are being formed at different times.

The TEM images obtained for colloid is shown in Fig.3. It is clear from the TEM images that the particle size, nearly spherical particles of average size 6.5 nm is obtained. The typical high resolution TEM image (Fig.3a) confirms the particles are spherical in shape.

The Scherrer rings, characteristic of fcc silver is clearly observed, showing that the structure seen in the TEM image are nano crystalline in nature. It is observed that the silver nanoparticles are scattered over the surface and no aggregates are noticed under TEM. The difference in size is possibly due to the fact that the nanoparticles are being formed at different times.

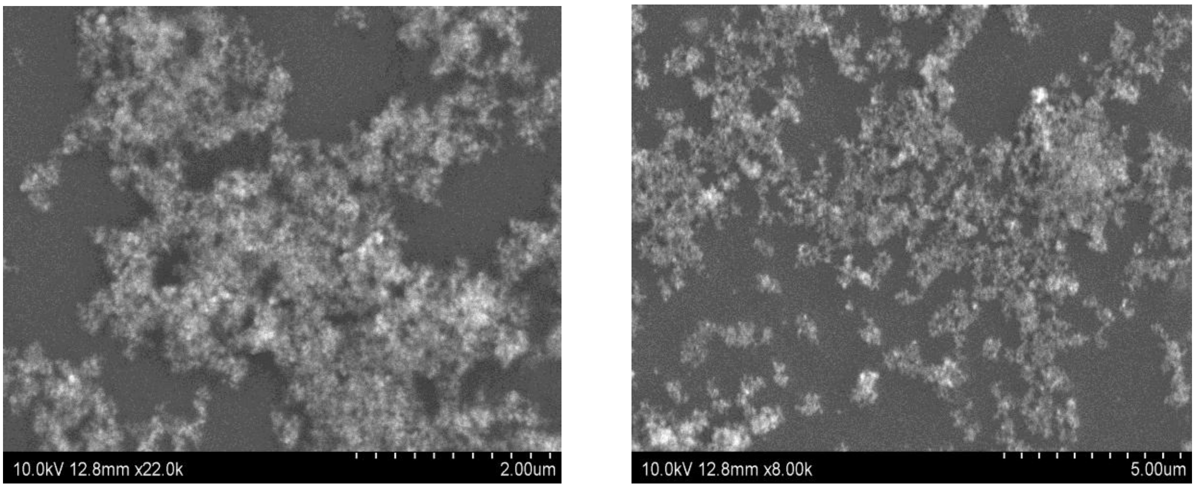


Fig 2: SEM images of 2-aminocyclopent-1-ene-1-carbodithioic acid onto a surface of silver Nanoparticles

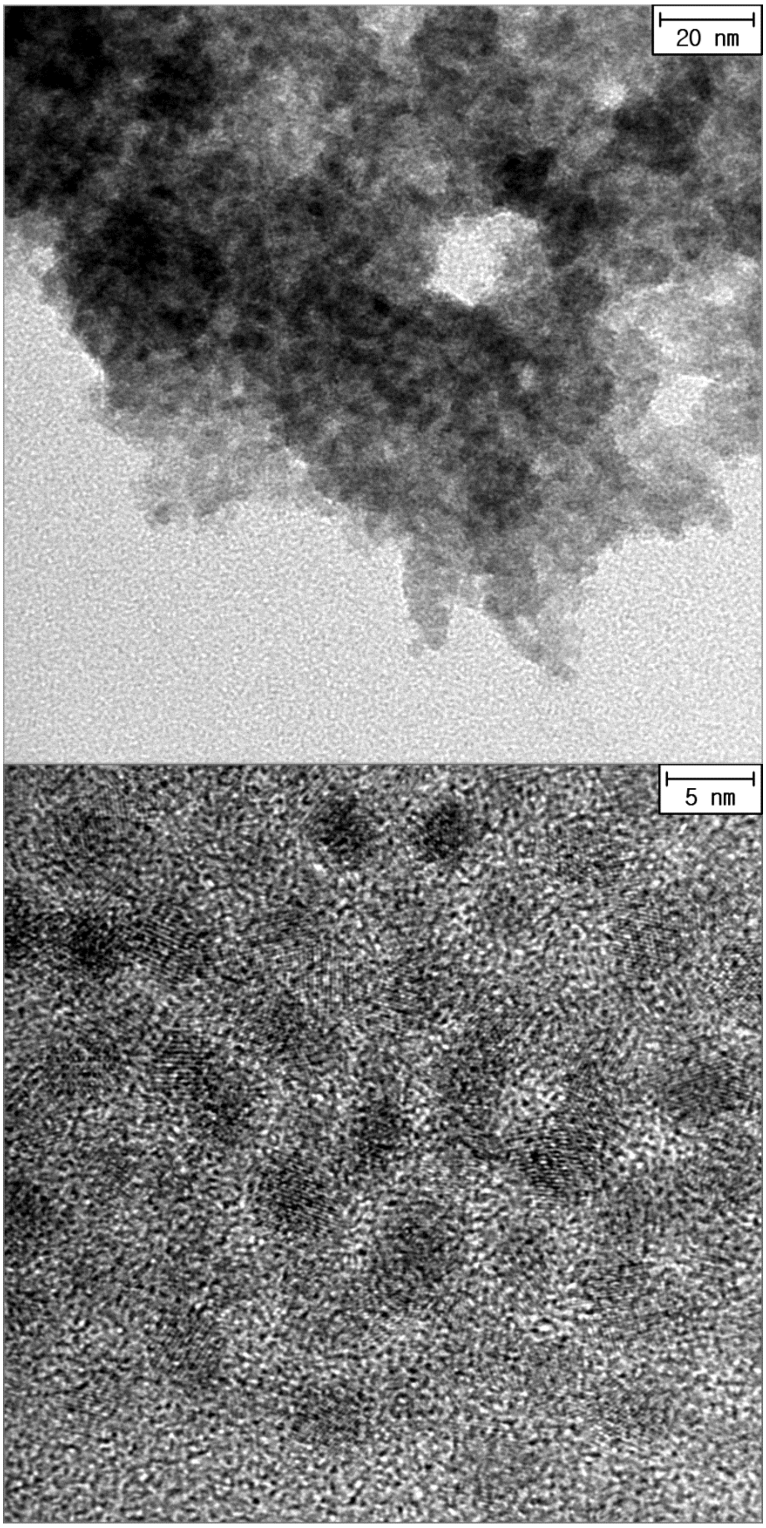
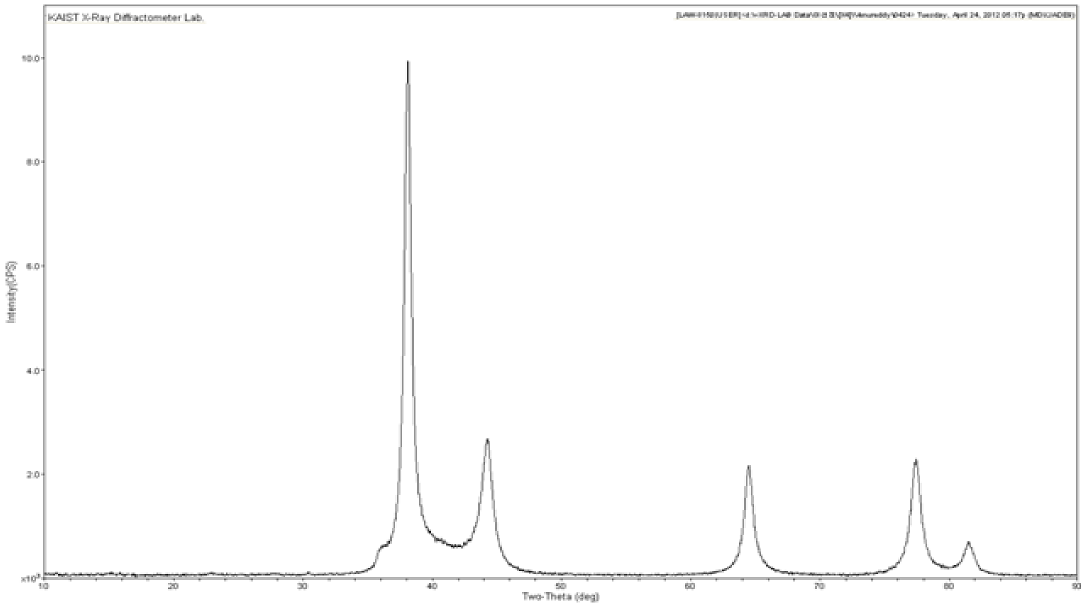


Figure 3: Transmission electron micrographs of the silver nanoparticles used in this work. (a) The bar marker represents 20 nm, (b) 5 nm

2.6. X-ray diffraction study:

The XRD spectrum confirms the tendency of nano particles to form the organized structures, as seen from the peaks in the small angle XRD spectrum in “Fig.”4. The peaks are broadened because of the nano crystalline nature of silver nanoparticles. By comparing with standard database values, all the peaks can be indexed to face-centered cubic (fcc) silver crystal structure. Three peaks at 2y values of 37.99, 62.843 and 75.462, correspond to the (1 1 1), (2 0 0) and (2 2 0) planes of silver nanoparticle, respectively.

The XRD of different particle sizes of Ag-NPs capped with 2-aminocyclopent-1-ene-1-carbodithioic acid prepared in water as solvent. From this figure, it can be noticed that the particles appeared basically amorphous and abroad. Size-dependent and structure-specific features in diffraction patterns can be quite striking in nano meter-sized particles. Small particles have fairly distinct diffraction patterns, both as a function of size and as a function of structure type. In general, regardless of structure, there is a steady evolution in the aspect of diffraction profiles: as particles become larger, abrupt changes do not occur, features grow continuously from the diffraction profile and more details are resolved. These observations form the basis for a direct technique of diffraction pattern analysis that can be used to obtain structural information from experimental diffraction data. The Ag-NPs are almost crystallized with the appearance of diffraction peaks at the scattering angles (2y) at 37-39, which could be indexed to the scattering from the planes (111), (200), (220) and (311), respectively, which is in agreement with the results of Leff et al. [15]. It is well known that with diminishing crystallite size the measured XRD pattern exhibits broadening, and very often overlapping reflections. The broadening of the reflections is inversely proportional to the crystallite size (i.e. size of coherently diffracting domains). The relation is known as Scherrer’s equation where “y” is the diffraction angle of a particular reflection. The total diffracted intensity for a given Bragg reflection from a crystallite is the sum of independently diffracted intensities by each of the unit-cell columns making-up the crystallite. It means that the calculated size distribution is in fact a distribution of diffraction column lengths in a given crystallographic direction perpendicular to the diffraction planes and not of crystallite (coherently diffracting domains) sizes. Theoretical considerations show that the interference function of a polycrystalline or nano crystalline solid is identical to that of an arrangement of isolated particles with the same size or size distribution as those of the polycrystalline or nano crystalline solid [16,17]. Thus the values of Scherrer’s formula are solely an estimate of a volume-weighed average column length. This explains the difference between the experimental and theoretical values, and the values from the Scherrer’s formula is termed ‘‘apparent crystallite size’’ [18].



“Fig.” 4: XRD patterns 2-aminocyclopent-1-ene-1-carbodithioic acid capped silver nanoparticles.

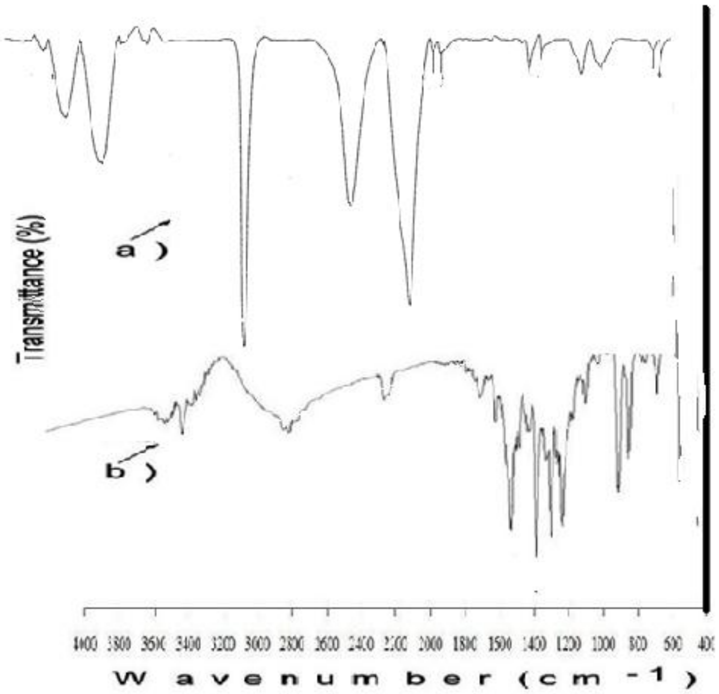
2.7 FT-IR analysis:

The IR spectra of the free 2-aminocyclopent-1-ene-1-carbodithioic acid and the particles capped by 2-aminocyclopent-1-ene-1-carbodithioic acid are given in Fig. 5. The IR spectra of the nano particles and the free 2-aminocyclopent-1-ene-1-carbodithioic acid molecule are similar to one another, indicating that the organic molecules have indeed become a part of the nano particles. However, are markable difference in the peak intensity is found between the peaks of IR spectra of free 2-aminocyclopent-1-ene-1-carbodithioic acid and 2-aminocyclopent-1-ene-1-carbodithioic acid capped Ag-NP in “Fig.”5. The reason for the intensity difference between the spectra is believed to be the thiolate molecules on the nano particle forming a relatively closely packed thiol layer and molecular motion being constrained [19].

Thus, this steric constraining effect on the transverse mode (rocking mode, wagging mode, etc.) is stronger than that on the longitudinal mode (stretching mode, etc). Therefore, the change of the peak intensity of the longitudinal modes is smaller than that of the transverse mode. The C–S stretching mode is due to the position of the C–S bond nearest to the surface of the silver particle, and a chemical bond can form between S and Ag atoms.

The FTIR spectrum of the nano crystals provides additional information about the local molecular environment of 2-aminocyclopent-1-ene-1-carbodithioic acid. The FTIR spectra of the free 2-aminocyclopent-1-ene-1-carbodithioic acid and Ag nanoparticle capped by 2-aminocyclopent-1-ene-1-carbodithioic acid thiol are represented in Fig. 4. From the spectrum of free 2-aminocyclopent-1-ene-1-carbodithioic acid thiol, it can be noticed that the azo group appeared at 1580 – 1650 cm^{-1}, respectively. The weak band appeared at 2360 cm^{-1} is attributed to the S–H stretching vibration mode[7]. The two bands appeared between 1380 and 1240 cm^{-1} are assigned to the stretching vibration of C-N group. The band appeared at 1627 - 1690 cm$^{–1}$ is attributed to the N-H primary stretching group. The band appeared at 756 cm^{-1} is assigned to C–S stretching mode [20]. Generally, the vibrational spectrum of Ag-NPs capped with 2-aminocyclopent-1-ene-1-carbodithioic acid thiol molecule is similar to the spectrum of 2-aminocyclopent-1-ene-1-carbodithioic acid thiol indicating that, the organic molecules have indeed become a part of the nanoparticles.

However, there is a remarkable difference in the peak intensity found between the peaks of the transverse mode (rocking mode, bending mode, etc.) in 2-aminocyclopent-1-ene-1-carbodithioic acid and Ag nanoparticles capped by 2-aminocyclopent-1-ene-1-carbodithioic acid. The reason for the intensity difference between the spectras is believed to be that the thiolate molecules on the nanoparticle form are relatively close packed thiol layer and molecular motion is constrained [21]. Thus, this steric constraining effect on the transverse mode is stronger than that on the longitudinal mode. Therefore, the change of the peak intensity of the longitudinal modes is smaller than that of the transverse mode. The small peak at 2360 cm^{-1} which corresponds to the S–H stretching vibration mode, disappears when the 2-aminocyclopent-1-ene-1-carbodithioic acid molecules adsorb on the silver particle surface (comparing spectra of free 2-aminocyclopent-1-ene-1-carbodithioic acid (4a) and Ag-NP capped by 2-aminocyclopent-1-ene-1-carbodithioic acid (4b), giving strong evidence that 2-aminocyclopent-1-ene-1-carbodithioic acid anchors on the silver surface through the sulfur atom in the mercapto group [22].



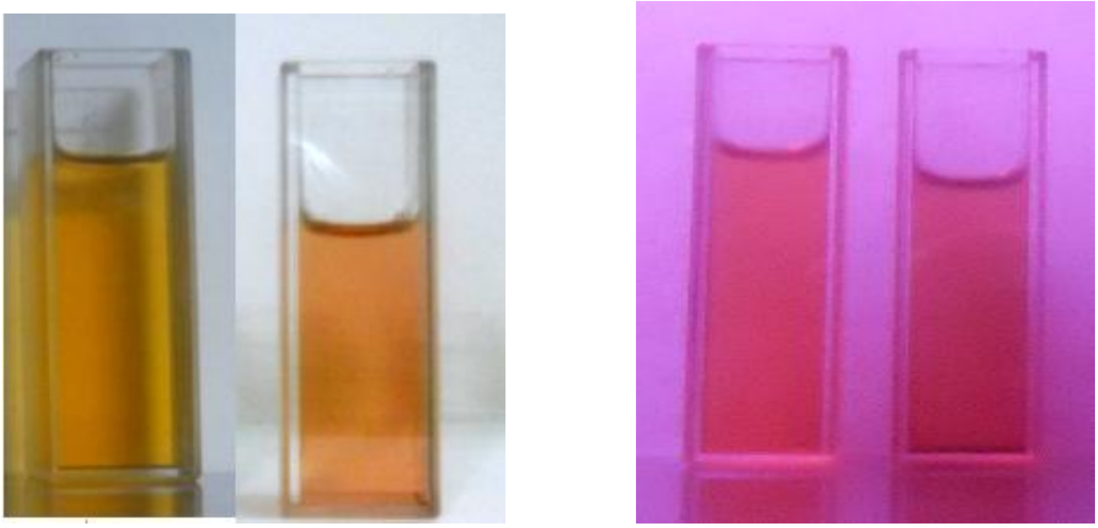
“Fig.” 5. FT-IR spectra of (a) 2-aminocyclopent-1-ene-1-carbodithioic acid; (b) 2-aminocyclopent-1-ene-1-carbodithioic acid capped AgNP;

III. Photophysical properties of the new ACA capped AgNPs:

3.1 Fluorescence emission spectra measurement:

The above synthesized 2-aminocyclopent-1-ene-1-carbodithioic acid capped Ag-NP (0.1mmoles) is dissolved in solvent DMSO to study their photoluminescence activity. “Fig” 6 shows the luminescence of 2-aminocyclopent-1-ene-1-carbodithioic acid (Left) & Ag-NP (Right) in DMSO at (a) daylight and (b) UV-lamp of 254 nm excitations respectively. Basing on this reference the fluorescence studies were carried to our synthesized silver nanomaterials. “Fig.” 7 and 8 shows the fluorescence emission spectra for synthesized silver nanoparticles. The emission spectra were recorded for these systems, in which fluorescence excitation wavelength was fixed.

Silver nanoparticles in DMSO showed fluorescence emissions at 522 nm. Whereas 2-aminocyclopent-1-ene-1-carbodithioic acid in DMSO showed 479 nm emission which is little bit lesser than the synthesized nanoparticles. From absorption and emission spectra’s the stokes shifts observed as 58nm. The detailed description with Stokes shifts were presented in table-4.



“Fig.” 6. Emission colors of fluorescent 2-aminocyclopent-1-ene-1-carbodithioic acid capped Ag-NP nanoclusters excited with a UV lamp (Left - In day light; Right – In UV lamp@254 nm) in DMSO solvent.

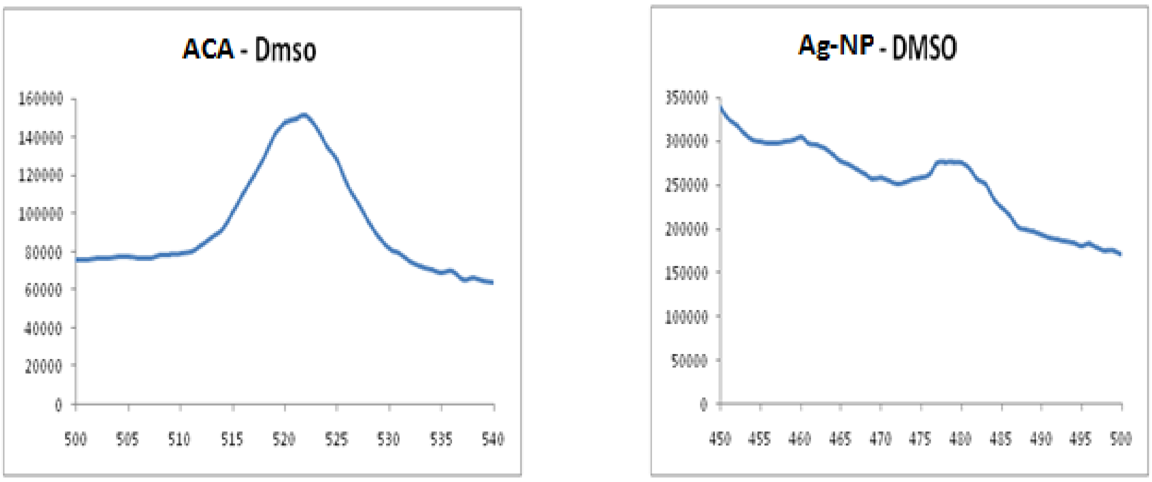


Fig. 7 & 8: Fluorescence spectra’s exhibited by 2-aminocyclopent-1-ene-1-carbodithioic acid & synthesized Ag-NP’s in DMSO solvent.

Table 5.5: Photophysical Data of 2-aminocyclopent-1-ene-1-carbodithioic acid (ACA) Capped AgNP’s:

Sl. no	Sample	Excitation wavelength (nm)	Emission wavelength (nm)	Stocks shift (nm)
1	**ACA**	**421**	**479**	**58**
2	**ACA-Ag-NP**	**452**	**522**	**70**

IV. CONCLUSION

ACA capped Ag-Nps are prepared by a simple, direct method. The progress of the reaction is observed through UV- Visible Spectrophotometric Studies. The Size & shape of nanoparticles are studied through SEM, TEM and XRD. From the study of Fluorescence spectra exhibited by 2-aminocyclopent-1-ene-1-carbodithioic acid & synthesized Ag-NP’s in DMSO solvent, it is clearly evident that these ACA Capped Ag-NPs are suitable biomarkers.

V. Acknowledgements

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