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Direct Synthesis and Stabilization of Bi-Sized Cysteine-Derived Gold Nanoparticles: Reduction Catalyst for Methylene Blue

Sirajuddin[a,*], A. Nafady[b], H.I. Afridi[a], S. Sara[a], A. Shah[c] and A. Niaz[c]
[a]*National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro, 76080, Pakistan*
[b]*Department of Chemistry, Suhag University, Egypt*
[c]*University of Science and Technology, Bannu, NWFP, Pakistan*

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Bi-sized and separable gold nanoparticles (AuNps) with smaller sizes were synthesized by treatment of cysteine with tetrachloroauric acid solution. These nanoparticles were made stable with further reduction in size after adding very small volume of NaOH solution before controlled heating. In NaOH treated solution the AuNps stopped precipitation as compared to untreated solution. Various methods such as UV-Vis spectroscopy, Transmission Electron Microscopy (TEM), X-ray Diffractometry (XRD), FTIR and Raman spectroscopy were used for characterization of surface properties and interaction between AuNps and cysteine. The results showed good correlation with literature regarding the interaction but interesting differences in size distribution as evident from high resolution TEM micrograph. Zeta potential studies revealed that these particles are negatively charged. Surprisingly, the Raman of the cysteine-derived AuNps without NaOH showed tremendous enhancement as compared to pure cysteine and cysteine-derived AuNps treated with NaOH. The NaOH treated Cyst-AuNps sol proved as excellent homogeneous catalyst for reduction of methylene blue (MB).

Keywords: Bi-sized gold nanoparticles, NaOH, Stabilization, SERS activity, Reduction of MB

INTRODUCTION

Since their discovery by Faraday [1] and investigation of dramatically different properties than bulk metal, AuNps have been thoroughly studied for several purposes such as catalysis [2] drug delivery [3] optics [4] sensor development [5] (Dai *et al*. 2004), architectural applications [6] *etc*. In most of synthetic procedures employed so far, the choice of capping agent plays very important role not only for attachment to AuNps but for their stabilization and further attachment to substrate. Among various types of AuNps reported so far, thiol derivatized particles are used by many researchers due to their high stability by forming Au-S bonds and good control over size distribution [7]. However, thiol capped AuNps especially those derived from alkanthiols have only one type of strong negative side (Au-S-) which if interacted with positive surface looses the actual functionality due to AuNps-surface interaction. So it is highly demanded for a capping molecule to have some additional positive and negative sides for attachment to specific substrate where AuNps are totally available for their functionality.

Cysteine is the molecule of choice for such type of strategic output of functionalized AuNps. Cysteine-capped AuNps are not newer in literature but in most of the cases they are not synthesized directly. A reducing agent usually $NaBH_4$ is first used for preparation of AuNps and then these particles

*Corresponding author. E-mail: drsiraj03@hotmail.com

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are interacted by treating with cysteine in solution or on surface [8-14]. The direct synthesis of Cysteine derived AuNps has been reported recently [15] however, the synthesized nanoparticles had the average size of >50 nm at lower pH and even 36 nm under extremely high pH of 12, respectively.

The activation of mild reducing agent [16] like cysteine needs the addition of heat or base catalyst. Moreover, being a biomolecule, cysteine has strong affinity for adsorption on surfaces of different metals, like gold, copper and silver [17]. Using such properties cysteine can be activated as reducing as well as capping agent to for AuNps by using free -COOH/ COO^-, NH_2/NH_3^+ or -SH/S^- groups. However, optimization of several parameters is required for the formation of stable cysteine derived gold nanoparticles. Availability of several groups on cysteine capped gold nanoparticles promises their strong interaction to electrode or other surface. This promises greater stability of AuNps at substrate and makes them suitable for application in catalysis and sensor studies.

EXPERIMENTAL

Cleaning of Glassware and Preparation of Solutions

Glassware was soaked in 3 M HNO_3 overnight. It was then washed with detergent solution followed by tape water and distilled water. Finally it was rinsed at least three times with Milli-Q water. All glassware was then dried in oven at 110 °C for 2 h and cooled to room temperature before use. All solutions were prepared in milli-Q water.

Chemicals and Solvents

Analytical grade tetrachlroauric acid ($HAuCl_4$) and methylene blue (MB) were purchased from Sigma-Aldrich Chemicals, while L-cysteine was from Merck. Other chemicals such as alkali, acids and salts were also of ultra-pure quality and purchased from different chemical companies.

Instrumentation

A Cary-Varian 5000 spectrophotometer was used for recording UV-Vis spectra. The instrument was first baseline corrected by putting blank (in 1 cm^2 quartz cell) in both compartments. After this the blank from working compartment was removed and working solution of AuNp put instead. The spectra of analytes were then observed between 400-700 nm in most cases. Zeta potential study of nanoparticles solution was performed on a Zeta Plus, Zeta Potential Analyzer of Brookhaven Instruments Corporation. TEM micrographs were recorded using a Philips CM20 of Oxford Instrument. A Spectrum RX1 of Perkin Elmer was used for FTIR spectra of the respective material in KBr discs. A Renishaw RM 2000 having 782 nm diode laser with Raman arrangement was used for Raman spectral analysis. A Phillips 1729 X-ray diffractrometer (XRD) with Cu KR radiation was used for Powder X-ray diffraction results.

Sample Preparation for XRD, IR and Raman Spectroscopy

Dried samples of AuNps were preferred in each case. According to procedure, fresh solutions containing AuNps treated with and without NaOH were poured separately in two big petri dishes and covered from dust with a ventilated cover. These solutions were let to dry and washed several times with water to remove any unreacted cysteine and other ions. After several washings the finally dried material in each case was scratched with a clean glass slide, made powder and collected in small sample bottles before analysis.

Preparation of Standard Gold Stock Solution

Gold solution of 770 ppm containing Au(III) ions was prepared from its analytical grade salt by dissolving appropriate quantity in 100 ml water in volumetric flask.

Stock Solutions of Cysteine and Sodium Hydroxide Solutions

0.5% Stock solution of cysteine was prepared form its analytical grade reagent in Milli-Q water. The flask containing solution thus prepared was put in a sonicator for at least two hours to ensure the complete dissolution of the reagent. Aqueous sodium hydroxide solution of 0.1 M concentration was prepared in milli-Q water by dissolving a little bit more than desired quantity. KHP standardization gave a value of 0.124 M from which 0.1 M NaOH was prepared by dilution procedure.

Synthesis of Cysteine-Capped AuNps

NaOH untreated AuNps were synthesized by taking 0.26 ml of standard gold solution followed by addition of 3.34 ml

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of water and 0.4 ml stock solution of cysteine in a sample tube. The sample bottle containing this mixture was heated on a hot plate already set at a temperature of 175 °C until the appearance of light red color in 2-3 min. The sample bottle was then cooled under running tape water to bring the mixture to room temperature. The same procedure was repeated for the synthesis of NaOH treated AuNps. However in this case, the same amount of gold solution was treated with 3.31 ml of water followed by 0.4 ml of stock solution of cysteine and 0.03 ml of 0.1 M NaOH.

Reduction of MB Dye

NaOH treated cyst-AuNps sol was used for reduction of MB solution. According to procedure 2 solutions of 10 µM MB, one without and another in the presence of 0.01 M $NaBH_4$ per 4 ml were analyzed by UV-Vis in the range of 450-750 nm. The catalytic properties of AuNps were checked by comparing the above spectra with those obtained after adding 0.05 to 0.2 ml of NaOH treated cyst-AuNps to solution containing 10 µM MB and 0.01 M $NaBH_4$ solution. Water was used as blank in each case.

RESULTS AND DISCUSSION

Optimization of Cysteine Concentration

Figure 1 describes the change in absorbance and λ_{max} of synthesized AuNps after addition of 0.05, 0.1, 0.15, 0.2, 0.3 and 0.4 ml of 0.5% cysteine solution represented by A, B, C, D, E and F, respectively. Analyses of samples were performed within 20-30 min after cooling to room temperature under tape water as per procedure given in Experimental section. The inset shows variation in color for mentioned solutions from light dark to bluish, violet and red.

It is seen that there is a continuous increase in the absorbance of AuNps from sample A to E with an abrupt drop in case of sample F. However there is a continuous blue shift in λ_{max} value of visible spectra by going from A to F with increase in the amount of cysteine. The blue shift in wavelength describes the decrease in size as well as aggregation of AuNps. A similar effect of decrease in size of AuNps with increasing ligand (citrate) has been described elsewhere [18]. However they used TEM to prove their results. The spectrum obtained for cysteine-capped AuNps is the

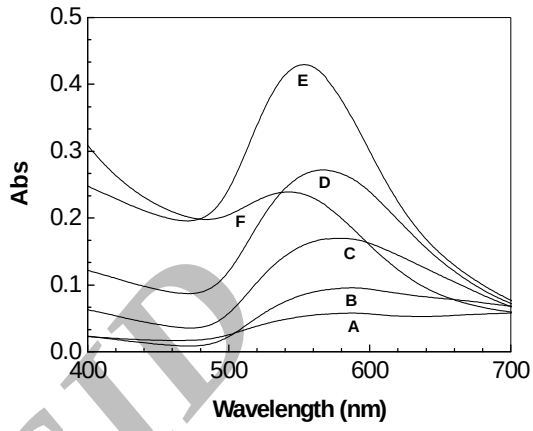

Fig. 1. UV-Vis spectra showing effect of concentration of cysteine on AuNps formation.

similar to the one obtained earlier [19]. However they capped AuNps with cysteine after reducing with $NaBH_4$ while direct capping with cysteine was true in our case. According to their argument the red shift and broadening of the surface plasmon band are observed when amino acids are added to the gold nanoparticles, indicating some consequent aggregation to surface modification of gold nanoparticles. During the current study, it was also observed that freshly prepared solution was quite stable but the particles precipitated to a considerable extent after 24 h.

Stabilization of AuNps in Solution with NaOH Addition

Fresh solution F from the above treatment was chosen for the effect of NaOH addition on the synthesis and stabilization of cysteine-capped AuNps in order to see if there is some effect on absorbance, shift of λ_{max} and stability of nanoparticles in solution. The spectra in the visible region were recorded and the results are shown in Fig. 2.

It is evident that there is a continuous blue shift of λ_{max} and decrease in the absorbance with increase in the volume of 0.1 M NaOH. The color variation from solution 1 to solution 5 (see inset) is also in good agreement with the mentioned observations. It was noted that except a very little precipitation in solution 1 and 2 other solutions showed no precipitation after 24 h. It means that NaOH has stabilized the AuNps inside solution. It has been reported that there is no aggregation, of

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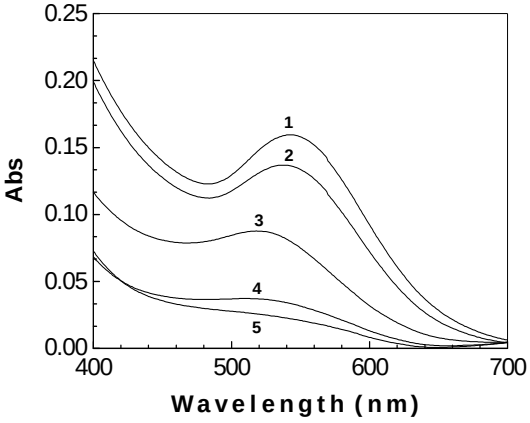

Fig. 2. Effect of variation of 0.1 M NaOH (0.01-0.05 ml) on synthesis of AuNps.

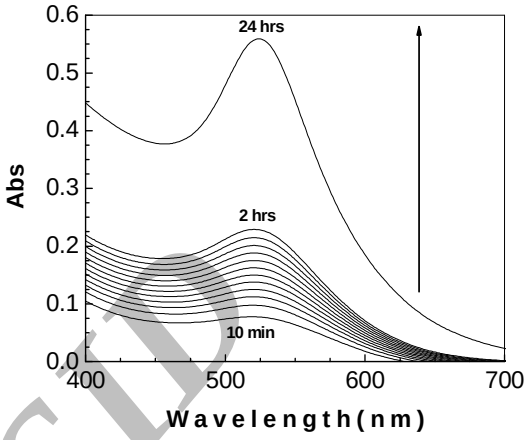

Fig. 3. UV-Vis spectra showing effect of time on formation of AuNps.

CALNN-capped gold above pH, 4 [20]. This is also true for solution 3 (pH, 4.3 ± 0.1) which was stable for more than 2 months despite its lower pH value. Moreover the solution 4 may be more stable than solution 3 and could contain very small particles however we chose solution 3 for further study due to its comparatively higher absorbance value. Another reason for stability of AuNps in solution in our case may be the heating of solution at higher temperature (175 °C) which can reverse the aggregation as reported [21] regarding the synthesis of cysteine-capped silver nanoparticles at 60 °C. In another report [22] $(Oct)_4N^{+-}Br$-protected gold nanoparticles were decomposed at 80 °C after thermal treatment of less than 3 h. But they also observed that thermal treatment of $(Oct)_4N^{+-}O_3SS$-protected gold nanoparticles at the same temperature for more than 17 h produced no effect on the intensity and wavelength of the gold surface plasmon band. They also showed that $(Oct)_4N^{+-}O_3SS$-protected gold nanoparticles do not decompose by the solid-state thermal treatment at 150 °C for up to 3 h. As in our case the heating at 175 °C was only for 2-3 min and no decomposition was observed so we can say that the nanoparticles were cysteine-capped and not disrupted by heat treatment. As the heating was constant both for AuNps with and without NaOH added solution so we say that of NaOH was the dominant factor responsible to stabilize AuNps in aqueous solution. $NaHCO_3$ has been used as stabilizing agent and modifier for size and size distribution of X-ray synthesized AuNps [3].

Effect of Time on Absorbance and λ_{max} of AuNps

Figure 3 describes the effect of time on the absorbance and shift in λ_{max} value of synthesized gold nanoparticles in NaOH treated solution 3.

A rapid increase followed by a slow decrease in absorbance proves that the rate of AuNps formation is dependant upon the number of available Au(III) ions as well as cysteine molecule. As one of these species (*e.g.* Au) is consumed with progress in time, hence a slower rate of AuNps formation is inevitable at later stage. In addition, a red shift of 6 nm (518-524 nm) for sample 3 as comparison to 10 nm (543-553 nm) for sample F (not shown) describes a very little aggregation in the former case. The rate of AuNps formation in case of sample F is extremely fast and reaches a maximum absorbance value in almost two hours along with further decrease after 24 h. This is why we observed precipitation of AuNps in solution F. The different trends of AuNps formation in solution 3 and solution F prove the stability of AuNps in former solution due to NaOH addition. The aggregation in case of cysteine-derived nanoparticles occurs due to hydrogen bond formation [23]. Electrolyte induced aggregation of cysteine-capped gold AuNps synthesized by borohydride method has already been mentioned earlier [8] however they have not mentioned the use of NaOH in their study. Time dependant study of cysteine capped nanoparticles has been reported by other workers [24] and reflects various aspects of the nanoparticles such as speed of reaction, aggregation,

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stability and rough idea about size.

TEM Characterization of AuNps

Figure 4 shows the TEM micrographs of sample F. Figure 4A represents the high resolution images of AuNps synthesized by cysteine only because the smaller particles could not be seen in low resolution image. Figure 4B shows an extended portion (red square) of Fig. 4A. Figures 4C and 4D are the corresponding size distributions for Figs. 4A and 4B, respectively.

Two types of particle distribution are observed here. The number of bigger AuNps is lower than smaller ones in the range of 23-50 nm with the most abundant particles possess a size of 34 nm. The estimated average size for bigger AuNps is 26.5 nm. Smaller AuNps have a size in the range of 2.4-8.6 nm with 33 nm as most abundant AuNps. An average size of 5.6 nm was true for the whole range of smaller particles. The overall average size of bigger and smaller AuNps was 16.05 nm. The two types of AuNps with 2 distinct size distributions can be easily separated in case a nano filter when mesh size of 20 nm is employed.

TEM images of cysteine-derived AuNps for NaOH treated sample 3 are shown in Fig. 5. Two different size distributions are also observed in this case. However, here the AuNps with larger size (Fig. 5A) have a range of 4.5-34.1 nm. The most abundant AuNps lie in the range of 9.1-8.2 nm. The average size of AuNps for the whole range is 17.4 nm. The size of smaller AuNps (Fig. 5B) ranges from 0.83-3.8 nm. The

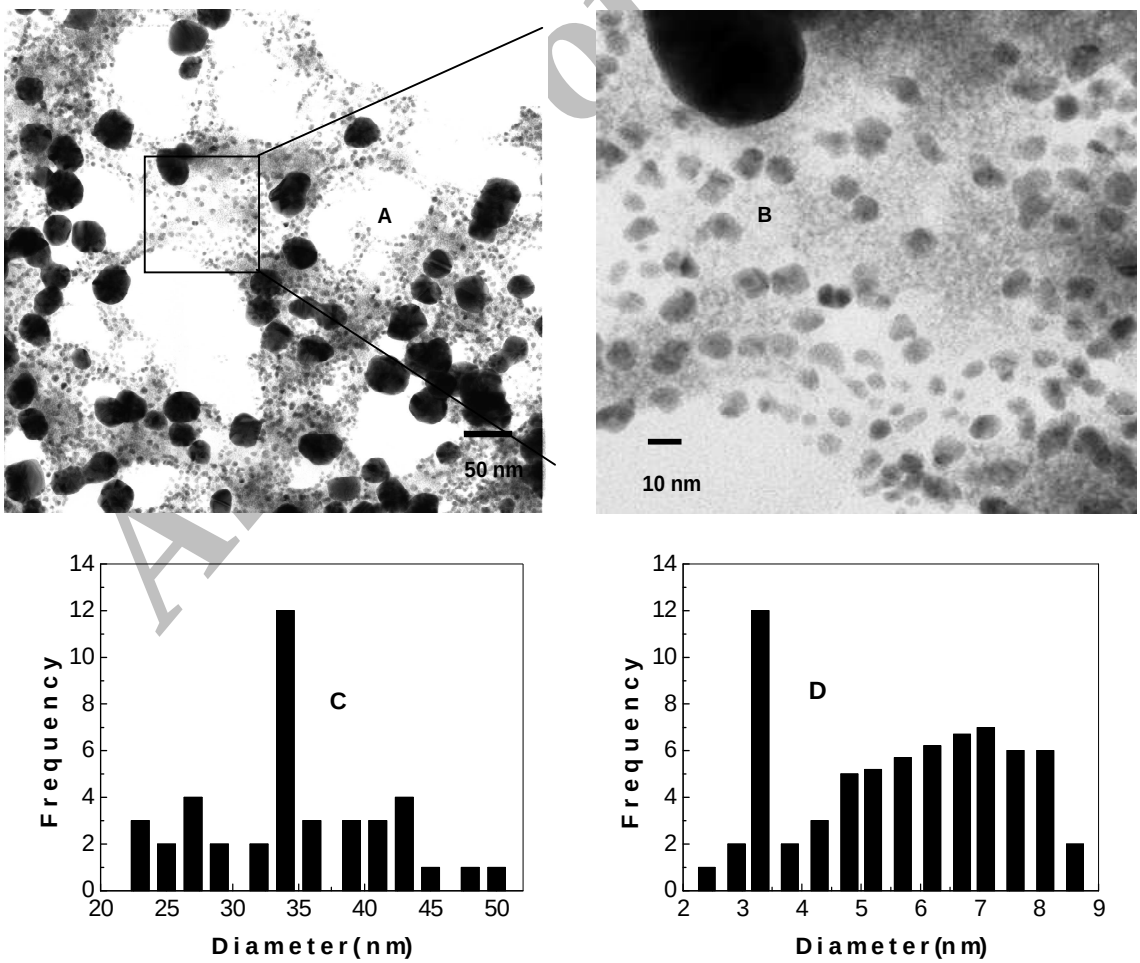

Fig. 4. TEM images and size distribution of cysteine capped AuNps for sample F.

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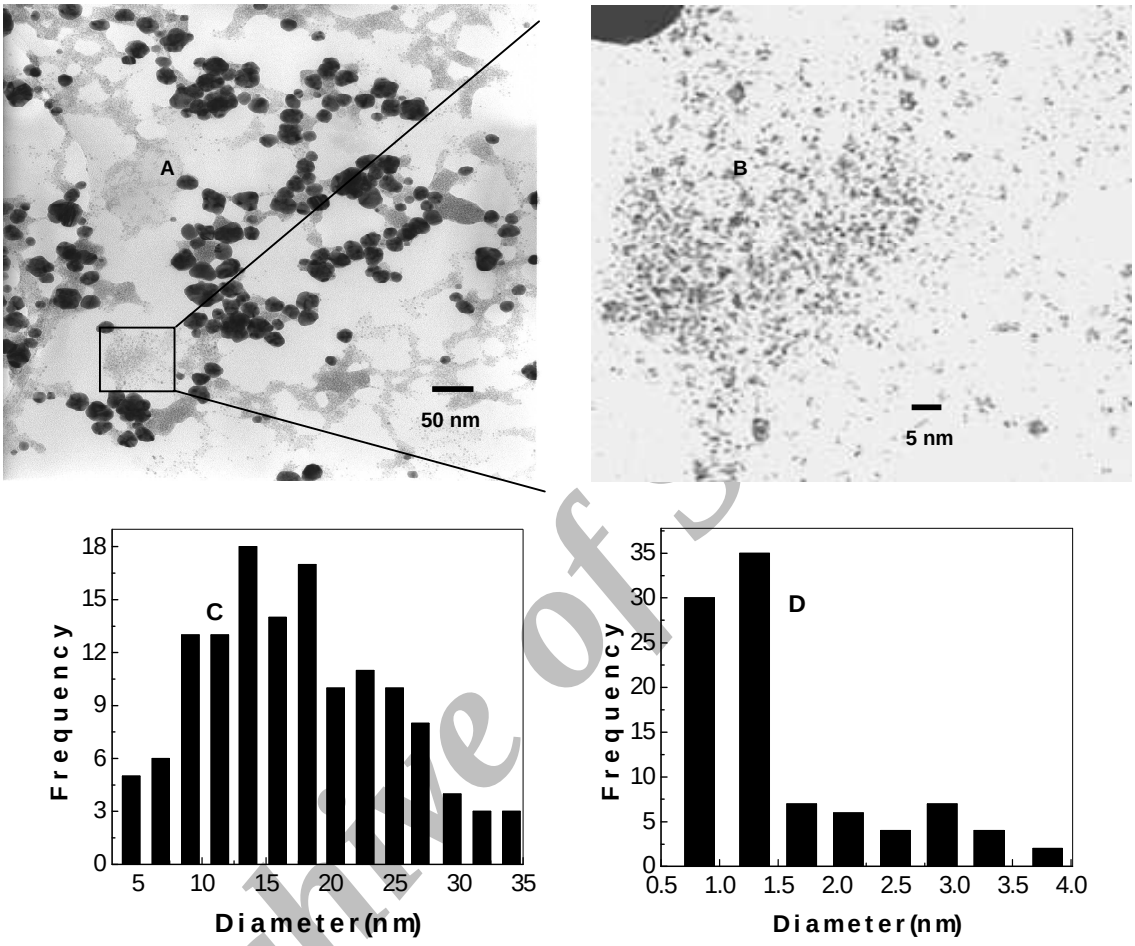

Fig. 5. TEM images and size distribution of cysteine capped AuNps for sample 3.

most abundant AuNps have the size of 1.3 nm followed by 0.83 nm. Even half nm particles could be watched in Fig. 5B, but could not be distinguished due to highly diffused nature. The average size of smaller AuNps is 1.5 nm. The overall average for both larger and smaller particles is, thus, about 9.5 nm. Corresponding size distributions for Figs. 5A and 5B are represented by Figs. 5C and 5D, respectively.

Two types of size distributions have also been observed [8] for cysteine-capped AuNps using borohydride method. There AuNps had the average size of 12 nm where the color of the solution changed from ruby red to blue because they first synthesized AuNps with borohydride and then added cysteine.

In contrast, we synthesize AuNps by directly treating Au solution with cysteine. The direct synthesis of cysteine derived AuNps has been reported elsewhere [15] however the average size of AuNps in that case was >50 nm with the exception of AuNps at pH 12 where the average size was 36 nm. Furthermore, bi-sized AuNps were not obtained in that instance. In our case the particles have an average size always < 36 nm. Comparing the TEM results of sample F with sample 3, the average particle size is the always smaller than the in latter case. This study verifies the results of UV-Vis spectral analysis, and highlights the role of NaOH as determining factor for size variation and stabilization of AuNps. Support to our study is the use of $NaHCO_3$ for inhibiting agglomeration and getting better size distribution in case of AuNps formation

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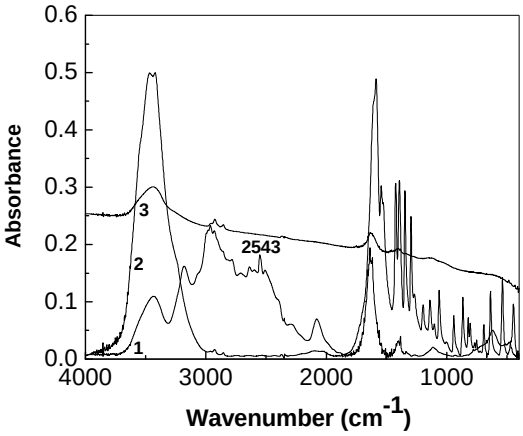

Fig. 6. IR spectra of cysteine (1), AuNps (2) and NaOH treated AuNps (3).

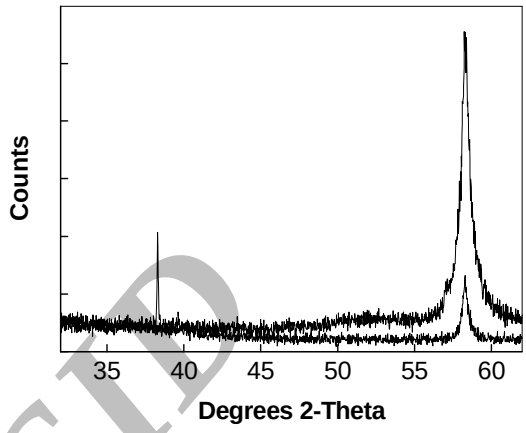

Fig. 7. XRD patterns of cysteine capped AuNps for solution F, below and solution 3, above.

[3]. In our case the average size modification of AuNps was improved from 16.05 to 9.5 nm after treating the solution with NaOH along with induced stability.

IR Studies

Figure 6 shows the IR spectra of cysteine, cyst-AuNps and NaOH stabilized cyst-AuNps. The results are quite similar with those reported earlier for cysteine derived silver nanoparticles [21]. The report confirmed the formation of S-Ag band in case of Cyst-AgNps by disappearance of band between 2545-2560 cm^{-1} (2543 cm^{-1} in our case).

Observations regarding the formation of S-Au bond have also been carried out by other workers [25] for cysteine adsorbed on gold surface. However in the previously mentioned study [19] the band between 3000-2800 cm^{-1} for CH stretching (present in our case) has not been discussed that was not observed in their spectra after AuNps formation. In another report [15] the broad band between 2300-3400 cm^{-1} represents the sum of intermolecular H-bonds resulting from NH_2 and OH of the cystine (formed after oligomerization of cysteine in water). Other bands in our study especially NaOH treated Cyst-AuNps can be explained in similar fashion as described by them.

XRD Characterization of AuNps

XRD patterns of AuNps formed in solution F and solution 3 in the 2θ range of 32°-62° are given in Fig. 7. A band is seen at 2θ = 58.3° in case of cyst-AuNps as well as NaOH treated cyst-AuNps. This peak may be related to substrate because gold crystalline faces appear at 2θ = 38.2° and 44.4° for plane (111) and (200), respectively in the studied region. However, in case of NaOH treated Cyst-AuNps, contribution from plane (111) of Au crystalline face at 2θ = 38.2° could be easily observed. So we say that the use of NaOH enhances the formation of crystalline patterns in cyst-AuNps.

XRD spectrum of C-Au-S with no crystalline faces of Au in the studied region has been reported [26]. However, they have described a band at 2θ angle of 56.2° from the silicon wafer substrate. According to them the absence of diffraction peak in C-Au-S is due to uniform distribution of gold atoms after reacting with sulfur.

Raman Studies of AuNps

Figure 8 describes the Raman spectra of pure cysteine, Cyst-AuNps and NaOH treated Cyst-AuNps in the range from 101-4000 cm^{-1}. It is clear that in case of pure cysteine molecule no SERS properties have been observed. On the other hand the NaOH treated Cyst-AuNps shows enhancement in peaks especially in the region from 101-2000 cm^{-1} with the peak showing SERS properties at 130.5 cm^{-1} corresponding to a peak of pure cysteine at 101 cm^{-1} which has been shifted after formation of AuNps. However the most interesting

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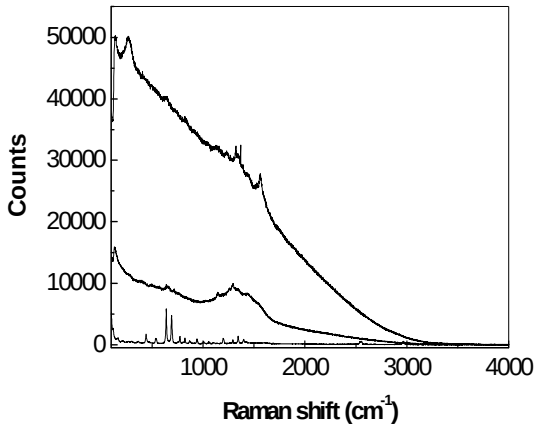

Fig. 8. Raman spectra of cysteine (below), NaOH treated cyst-AuNps (middle) and cyst-AuNps (above).

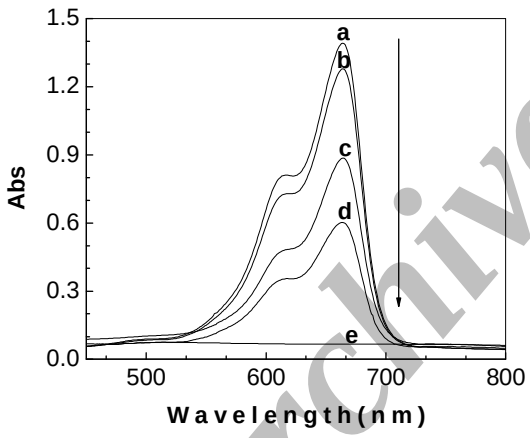

Fig. 9. Visible spectra of; 10 µM MB a), a with 0.01 M $NaBH_4$ b), b in the presence of, 0.05 ml c) 0.1 ml d) and 0.2 ml e) respectively of NaOH treated AuNps sol.

results are true in case of Cyst-AuNps formed without any addition of NaOH. Here the peak at 101 cm^{-1} in the pure cysteine shows a shift to 140 cm^{-1} after capping with AuNps. Another peak at 265 cm^{-1} which is not present (or obscured) in NaOH treated Cyst-AuNps also appears in untreated Cyst-AuNps sample. Some authors [27] have reported gold nano flowers as SERS sensor for 2-thiouracil with the best enhancement of signal at 920 cm^{-1}.

Regarding the characterization of AuNps it is observed that the strong signal related to S-H stretching at 2546 cm^{-1} is not observed in case of spectra for cyst-AuNps and NaOH treated cyst-AuNps samples. Similar results have been described elsewhere [19] for cysteine and cysteine capped AuNps. However in their case the AuNps were prepared by using $NaBH_4$ as reducing agent and then capping with cysteine. We used Cysteine as reducing as well as capping agent hence our study results in better SERS activity for cysteine after capping with AuNps.

Charge on AuNps

Charge on cyst-AuNps and NaOH treated cyst-AuNps was investigated by using zeta potential analyzer and the results are presented in Tables 1 and 2. It is seen that the cyst-AuNps have highest value of negative charge as compared to NaOH treated cyst-AuNps. This is due to difference in surface properties of two types of AuNps.

Application of NaOH Treated Cys-AuNps as Reduction Catalyst for MB

NaOH treated Cyst-AuNps solution as homogeneous catalyst was tested by taking its varying amount for MB reduction in the presence of $NaBH_4$ (Fig. 9). Each spectrum was noted after 5 min interval. It is observed that in the presence 0.01 M $NaBH_4$ there is little reduction (~9%) of 10 µM MB solution (spectrum b). However, after addition of 0.05 ml, 0.1 ml and 0.2 ml of NaOH treated cyst-AuNps sol, the reduction of MB reached to 38%, 56% and 100%, respectively in 5 min.

Catalytic reduction of MB by silver and gold nanocluster has been reported by other workers [28] however they used this strategy for determination of arsenic in water samples. Reduction of dye (Eosin) by AuNps has also been cited elsewhere [29] using UV-Vis spectrometry. The catalytic reduction of NaOH treated cyst-AuNps can be extended to other dyes and may be fruitful for control of environmental pollution and recycling technology in textile and dye industries.

CONCLUSIONS

The mentioned work describes the direct formation of cysteine-derived AuNps with 2 size distributions. It has been

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Table 1. Zeta Potential Value (Charge) of Cyst-AuNps

Run	Mobility	Zeta potential (mV)
1	-1.33	-17.00
2	-1.44	-18.48
3	-2.09	-26.69
4	-1.77	-22.67
5	-1.69	-21.59
Mean	-1.66	-21.29
Std. error	0.13	1.69
Combined	-1.66	-21.27

Table 2. Zeta Potential Value (Charge) of NaOH Treated Cyst-AuNps

Run	Mobility	Zeta potential (mV)
1	-0.21	-2.67
2	-0.15	-1.87
3	-0.13	-1.62
4	-0.53	-6.73
5	-0.22	-2.83
Mean	-0.25	-3.15
Std. error	0.07	0.97
Combined	-0.15	-1.87

concluded that controlled addition of NaOH induces stabilization of cyst-AuNps for a long time with decrease in size of particles as compared to untreated solution of cyst-AuNps. The cyst-AuNps shows better SERS activities for cysteine as compared to NaOH treated cyst-AuNps. NaOH treated cyst-AuNps proved as best reduction catalyst for MB and this study could find application in controlling of environmental pollution caused by dye discharging industries. The highly negative charge on cyst-AuNps proves them as better candidates for interaction with positive and neutral substrates.

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