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pH Effect on the Adsorption of Amino Acids on Gold Nanoparticles

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Abstract—*To understand the interactions of gold nanoparticles with amino acids, a complete study has been done at variable range of pH 5, 7, 9 and 11. Citrate capped gold nanopaerticles are synthesized and capped with three amino acids, L-Cysteine, L-Glutamic acid and L-Arginine. The amino acids interactions have been investigated with UV-Vis spectroscopy and surface plasmon resonance maximum values (λ_{max}) are analyzed. Within the limitations of the approach, the results indicate that L-Cysteine is most effective in replacing the citrate, L-Arginine least and L-Glutamic acid being intermediate. L-Cysteine coated gold nanoparticles also shows remarkable pH responsive behavior as compared to L-Glutamic acid and L-Arginine coated gold nanoparticles.*

1. INTRODUCTION

Noble metal nanoparticles (NPs) have been intensively studied in the past few years due to their unique properties. They exhibit strong absorptions in the visible region due to surface plasmon resonance (SPR), highly stable dispersion, chemical inertness and unique biocompatibility [1-2]. For such properties, stable gold nanoparticles (Au NPs) in solution are synthesized by coating its surface with different ligands [3].Gold surfaces are also suitable for studying peptide-peptide [4] or protein-protein [5] interactions using SPR spectroscopy. Amino acids (AAs) are considered as suitable agents in the biofunctionalization of Au NPs, as protective layers and for their assembly, due to the presence of different functional groups, such as –SH and –NH2, with affinity for gold. Therefore, an understanding of the role of functional groups of amino acids towards Au is necessary. L-Cysteine, is a promising compound to be used in this study for biofunctionalization of Au NPs and for the mediation of their assembly with gold surfaces [6]. Even more, AA capped gold surfaces are considered to represent the simplest mimics for protein surfaces [7]. There are many reports are available for synthesis of Au NPs using AAs as the capping agents and reducing agents [8]. But few reports [6, 9] are available to explain the aggregation behavior of AA capped Au NPs over a wide range of pH. In the present investigation, the Au NPs are synthesized using sodium borohydride as reducing agent and trisodium citrate as capping agent and the prepared Au NPs are then capped with variably functionalized AA and their aggregation behavior is studied over a complete pH range from 5 to 11 with time. Moreover, a comparative study of different AA especially acidic, basic and thiol containing conjugated Au NPs are also studied at variable pH conditions which lead to complete understanding of their interaction with Au NPs.

2. EXPERIMENTAL SECTION

2.1 Materials and Synthesis

L-Cysteine, L-Arginine and L-Glutamic acid, Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4.3H_2O$), Tri-sodium citrate, Sodium borohydride, were purchased from Sigma Aldrich, India. The pH of the Au colloidal solution and of amino acid solutions is adjusted separately using 1N HCl and 1N NaOH.

Colloidal solution of Au NPs of concentration 0.5mM is prepared. In a typical synthesis, 25ml of the 0.5mM $HAuCl_4$ is mixed with 5mM tri-sodium citrate in triply distilled water. This solution is then vigorously stirred for 30 minutes. To this solution, 0.6ml of freshly prepared $NaBH_4$ having concentration 0.002M is added drop wise with constant stirring for about 1minute. This prepared solution is then kept undisturbed overnight. This prepared solution is characterized using UV-Vis spectrometer showing SPB at approximately 520 nm.

2.2 Preparation of AA solutions and AA conjugated Au NPs

All the three AAs (L-Arginine (Arg), L-Glutamic acid (Glu) and L-Cysteine (Cys)) of concentration 1mM are prepared separately in triply distilled water. 1mM of each AA is taken in four separate 20 ml vials. The pH of each vial is adjusted as 5, 7, 9 and 11 respectively. Similarly the Au sol is also taken in four vials and pH of each is adjusted as 5, 7, 9 and 11 respectively. The Au colloidal solution and the AA with adjusted pH separately are then mixed in 9:1(v/v) ratio respectively. The time effect is measured with UV-visible

spectrometer at a resolution of 1nm and within the 200nm-800nm wavelength range.

3. RESULTS AND DISCUSSION

3.1 Structure and Morphology

The Au sol is stabilized by anionic citrate molecules, which are adsorbed on the positively charged Au NPs surface at different pH values, where citrate molecules itself undergo protonation. On addition of Cys at pH 5 to 11, the thiol group undergoes strong and thermodynamically favorable covalent bond formation with Au surface. To understand the role of Cys in the colloidal Cit-Au NPs sol, a complete picture can be evaluated from wavelength versus time (Fig. 1) and intensity @ 540nm versus time (Fig. 2) plots at different pH of Cys-Au NPs. At pH5, 7 (Fig. 1), SPR peak increases from 540nm to 566nm and from 537nm to 561nm, respectively. Further at pH 9, 11(Fig. 1), SPR peak increase from 526nm to 538nm and 528nm to 544nm, respectively. The more increase of λ_{max} with time are associated with aggregation at pH5 and pH7. Moreover, at pH5 and pH7 plasmon coupling occurs due to the formation of inter NP bridges due to H-bonding between NH_3^+ present on one Cys-Au NPs surface and COO- of other Cys-Au NPs surface. Further on additions of Cys at pH9 and pH11, -SH group will replace citrate group, thus absorbed on the surface of Au NPs and NH_2 (due to pH9, 11) and COO- groups will remain the surface. Fig. 2 shows the change in intensity@540nm versus time plot. Both the plots wavelength and intensity versus time support each other. As wavelength increases, intensity of the corresponding pH of Cys-Au NPs samples decreases, which is associated with the displacement of citrate molecules with –SH group of Cys at various pH values.

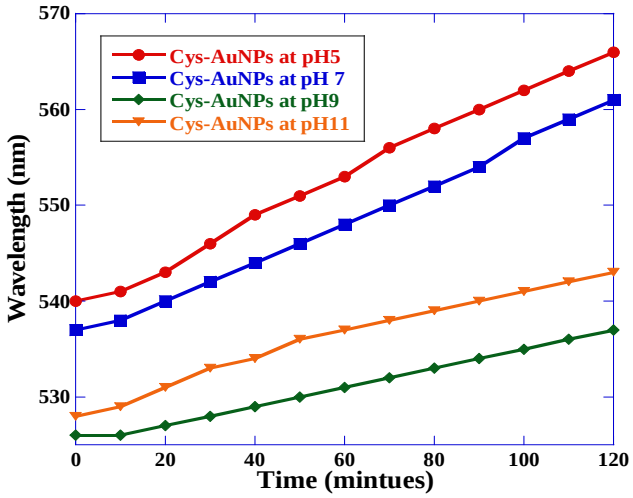

Fig. 1: Wavelength versus reaction time plot of Cys-Au NPs at different value of pH.

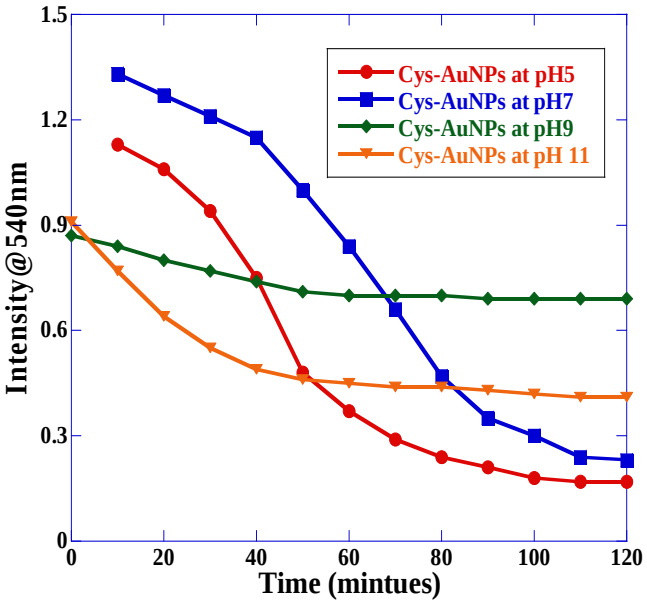

FIG. 2: Intensity@540nm versus reaction time plot of Cys-Au NPs at different value of pH.

In Arg-Au NPs and Glu-Au NPs, SPB remains same ~ 520 nm at all pH values (Fig. 3). Moreover, at a particular pH, there is no change in wavelength with time (Fig. 4), which indicates that Arg-Au NPs and Glu-Au NPs are more stable. In the case of Glu-Au NPs, no aggregation is seen at various pH values from 5 to 11. This may be attributed to two COO- groups of Glu, which stabilize the Au NPs with similar interactions as COO- groups of Cit molecule adsorbed on Au NPs surface. Similarly, in the case of Arg-Au NPs, one of the amine acts as primary amine can interact with Au NPs again through weak covalent bonds along with COO- of Arg and Cit molecules.

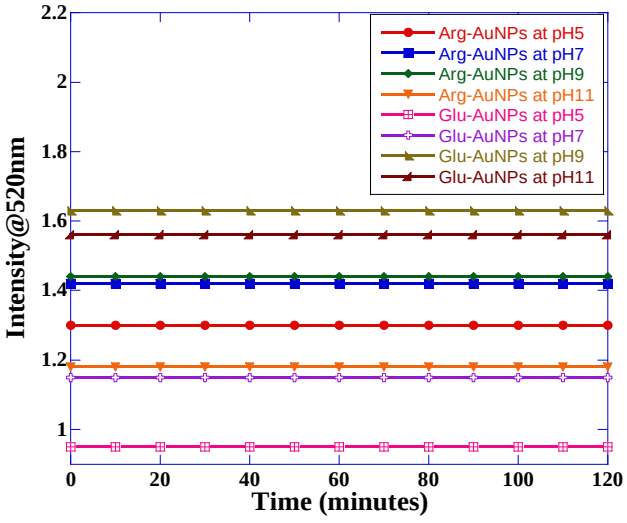

FIG. 3: Intensity@520nm versus reaction time plot of Arg-Au NPs and Glu-Au NPs at different value of pH.

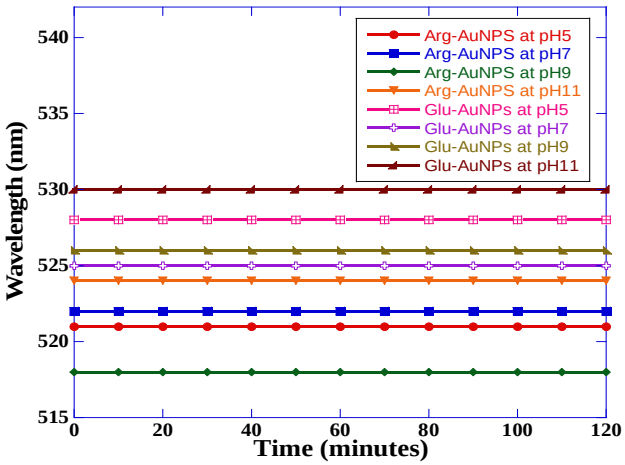

FIG. 4: Wavelength versus reaction time plot of Arg-Au NPs and Glu-Au NPs at different value of pH.

4. CONCLUSION

We report a simple interaction of AA with Au NPs at different pH values (5, 7, 9, and 11). Cys undergoes strong and thermodynamically favorable covalent bond formation with Au surface because of the presence of –SH group, independent of pH. It may allow the desorption of citrate from Au NPs leading to different extent of aggregation depending upon pH of the media. No aggregation is observed in the case of Glu-Au NPs and Arg-Au NPs because of weaker covalent interactions of $–NH_2$ group.

5. ACKNOWLEDGEMENTS

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