

SYNTHESIS OF GOLD NANOPARTICLES AND INTERACTION WITH AN ORGANIC DYE UNDER VARYING PH CONDITIONS: A UV-VISIBLE SPECTROSCOPIC STUDY

Arijit Bisharad^{1*}, Sontara Konwar Boruah¹

¹*Dept. of Chemistry, School of Fundamental and Applied Sciences, Assam Don Bosco University, Guwahati-782402*

*For correspondence: (arijit.bisharad@dbuniversity.ac.in)

Abstract: Gold nanoparticles or shortened as AuNPs possess unique optical and physicochemical properties, enabling them to be used in various applications such as in sensing, catalysis, photonics, and biomedical systems. In this study, gold nanoparticles were synthesized by the Turkevich citrate reduction method and their interaction with sodium fluorescein (NaFl) was investigated by UV-Visible spectroscopy under varying pH conditions. Spherical AuNPs have been seen to exhibit a surface plasmon resonance (SPR) peak in the 530–543nm region. Interaction studies revealed that sodium fluorescein demonstrated pH-dependent interaction, with clear evidence of dimer formation and enhanced adsorption onto the AuNP surface at alkaline pH (pH 9.2). This result highlights the interaction behaviour of structurally and functionally different organic dyes with gold nanoparticles, emphasizing the critical role of dye charge, structures of the molecules, and the pH of the solutions in governing nanoparticle-dye interactions.

Keywords: Gold nanoparticles; UV-Visible spectroscopy; Sodium fluorescein; pH effect.

1. Introduction:

Nanotechnology deals with materials in the size range of 1–100 nm, where the confinement of electrons leads to unique optical, catalytic, and electronic properties [1-5, 6]. Among metallic nanoparticles, gold nanoparticles (AuNPs) are one of the most extensively studied due to their excellent chemical stability, biocompatibility, size-tunable surface plasmon resonance (SPR), and facile synthesis [7-9]. The Turkevich citrate reduction method is the most classic and widely used method to synthesize spherical AuNPs. Citrate acts as both the reducing and stabilizing agent, yielding colloidal gold with a characteristic red to wine-red colour due to SPR absorption around 520–550 nm [10-13]. Organic dyes such as sodium fluorescein (NaFl) have broad applications in analytical chemistry, textiles, biology, and environmental science [14-16]. Diverse interactions with metallic nanoparticle surfaces can be examined and studied thanks to their molecular charge and structure. Sodium fluorescein (NaFl) is a pH-sensitive xanthene dye known for strong fluorescence and structural transformation across pH [17,18]. Understanding how dyes interact with AuNPs is essential for designing advanced sensors, catalytic systems, and photophysical probes. Fluorescein provides an excellent model for contrasting electrostatic, spectroscopic, and pH-dependent behaviours.

2. Experimental Section:

2.1. Materials:

Chloroauric acid (HAuCl_4), trisodium citrate, sodium fluorescein, and all other reagents were of analytical grade. Milli-Q distilled water was used for all preparations.

2.2. Synthesis of Gold Nanoparticles:

The trisodium citrate acts as the reducing agent for the reduction of gold from +3 oxidation state to 0 oxidation state. For the preparation of gold nanoparticles, 0.0009821M AuCl_3 stock solution in 25 ml volumetric flask (Solution A) and 0.01M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ solution i.e. 0.2580 gm $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ in 100 ml of deionised water (naming it as Solution B) were prepared. The molar ratio of AuCl_3 : $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ should be 1:7. Then, 4ml of Solution A was taken in a 10 ml volumetric flask and to this 2.744 ml of Solution B was added. The mixture was shaken well and was then diluted with deionised water up to the mark. This mixture is then transferred to an Erlenmeyer flask and is heated at 100°C in a water bath with constant stirring. Small pieces of aluminium foil were placed over the neck

of the flask to prevent excess evaporation and boil over. It was heated for almost 30 minutes or until there is a gradual change in the colour from transparent to faint purple and then finally to ruby red colour, hence confirming the formation of gold nanoparticles. Quenching of the solution was followed by sonication for 15 minutes in a water bath. The synthesized AuNPs were stored at room temperature till further processing.

2.3. Preparation of Dye–AuNP Interaction Systems:

Sodium Fluorescein–AuNP System: 10^{-3} M sodium fluorescein dye solution was prepared by dissolving 0.0376 gm of sodium fluorescein dye mixed in 100ml distilled water. This was then preserved as stock solution for further usage. Thereafter, three different solution mixtures were made: (A) 1ml 10^{-3} M sodium fluorescein dye stock solution + 8.5ml pH 4 buffer solution + 0.5ml of AuNPs, then sonicated for 10 minutes (B) 1ml 10^{-3} M sodium fluorescein dye stock solution + 8.5ml pH 7 buffer solution + 0.5ml of AuNPs, then sonicated for 10 minutes (C) 1ml 10^{-3} M sodium fluorescein dye stock solution + 8.5ml pH 9.2 buffer solution + 0.5ml of AuNPs, then sonicated for 10 minutes.

2.4. UV–Visible Spectroscopy:

The UV-Visible spectra of sodium fluorescein at pH 4 showed two absorptions bands at 441.2nm and 460nm. These two peaks were due to the presence of neutral form fluorescein molecule (Figure 1, top). At pH 7, sodium fluorescein exhibits several absorption bands at 230nm, 275nm, 315nm and 490nm [19]. The UV-Visible absorption band at 490nm is due to the presence of monoanion form fluorescein molecule (Figure 1, middle). The UV-Visible spectra of fluorescein at pH 9.2 shows absorption bands at 230nm, 275nm, 315nm and 488nm. The UV-Visible band at 488nm is due to the presence of dianion form fluorescein molecule (Figure 1, bottom).

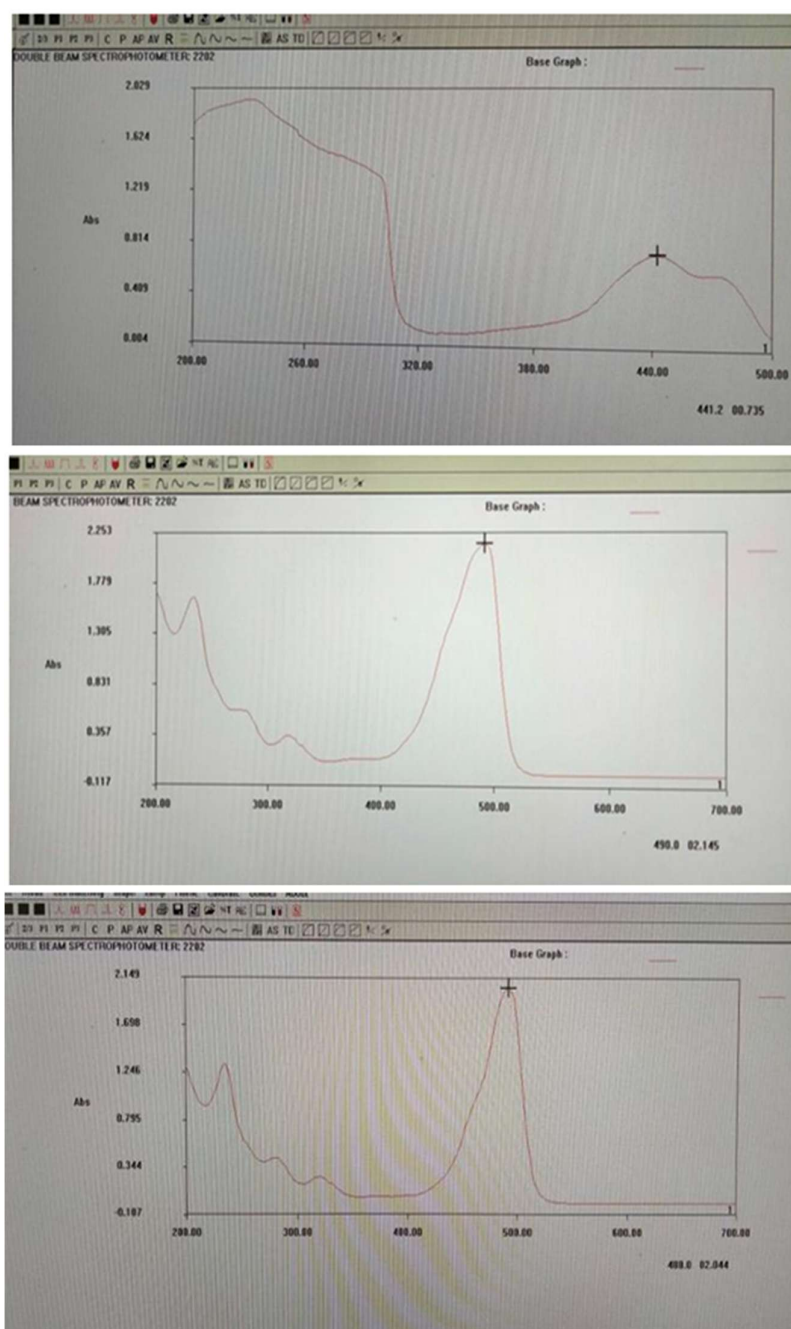


Figure 1: UV-Visible spectra of 10^{-3}M sodium fluorescein solutions at pH 4 (top), at pH 7 (middle) and at pH 9.2 (bottom)

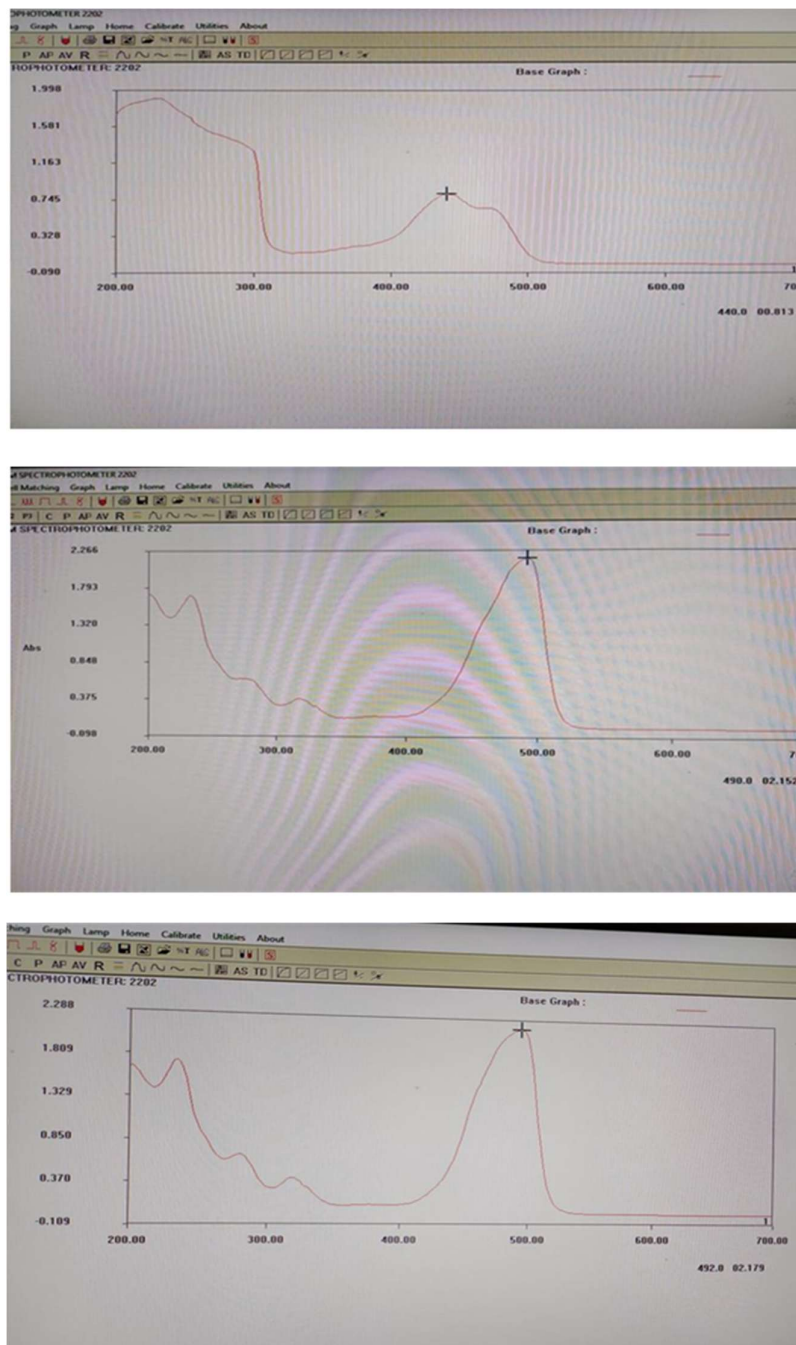


Figure 2: UV-Visible spectra of sodium fluorescein – AuNPs solution at pH 4 (top), at pH 7 (middle) and at pH 9.2 (bottom)

Upon spectroscopic reading, it was seen that the UV-Visible spectra of sodium fluorescein-AuNPs at pH 4 showed absorption band at 441nm. While the UV-Visible spectra of sodium fluorescein-AuNPs at pH 7 showed absorption band at 490nm. The UV-Visible spectra of sodium fluorescein dye at pH 9.2 showed absorption band at 492nm (Figure 3.6). At pH 9.2, there was a slight red-shift when sodium fluorescein solution was added to AuNPs. The spectral red-shift suggests that the dianionic fluorescein molecule is stabilized and forms dimers when adsorbed onto the nano surface of spherical AuNPs. The occurrence of hydrogen bonding interaction

between two neighbouring dianionic fluorescein molecules when adsorbed onto the nano sphere of AuNPs results the dimeric formation [20, 21]. The enhancement in UV-Visible absorption at 492nm was also observed for dianionic fluorescein molecules. This suggests that the dianionic fluorescein molecules were able to absorb onto the spherical nano surface of AuNPs. On the other hand, these effects were not observed by changing in spectral properties when sodium fluorescein solutions at pH 4 and pH 7 were added to AuNPs. The reason may be that, there were no communication of neutral and monoanionic fluorescein molecules with the AuNPs, presumably due to electrostatic repulsion.

3. Results and Discussion:

3.1. Characterization of Gold Nanoparticles:

The synthesized gold nanoparticles displayed the classical SPR band near 530–543 nm, characteristic of spherical AuNPs. SEM image confirmed the nearly spherical morphology expected from citrate reduction. The intense SPR peak confirms nanoparticle stability and the absence of aggregation in the as-prepared colloidal solution.

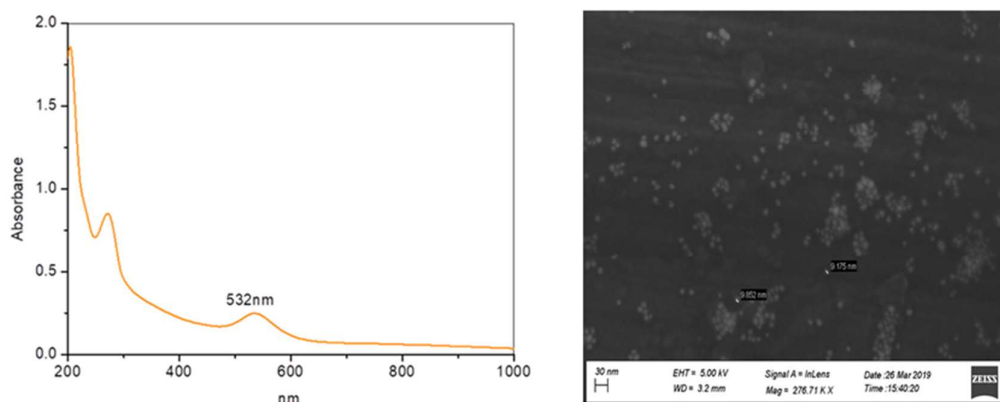


Figure 3: UV-vis spectra of AuNPs (left) and SEM image of the AuNPs (right)

3.2. pH-Dependent Behaviour of Sodium Fluorescein:

Sodium fluorescein has been seen to exist in multiple prototropic forms, namely—cationic, neutral, monoanionic, and dianionic. The nature of existence depends on pH.

3.2.1. Fluorescein at Different pH:

- At pH 4: Mostly neutral/lactone form; low absorbance.
- At pH 7: Monoanionic/dianionic mixture; increased absorbance.
- At pH 9.2: Predominantly dianionic form; strong absorption and fluorescence.

3.3. Interaction of Fluorescein with AuNPs:

3.3.1. UV–Visible Spectroscopic Changes:

Upon addition of AuNPs:

- At pH 4: Minimal change; weak interaction.
- At pH 7: Slight absorbance modifications, moderate interaction.
- At pH 9.2: Significant spectral changes indicating dimerization and adsorption of fluorescein on AuNP surfaces.

These effects are visible through: Shifts in the fluorescein absorption maxima, decrease in the AuNP SPR intensity and broadening of absorbance bands.

3.3.2. Mechanistic Interpretation:

At higher pH: Dianionic fluorescein strongly interacts with positively polarized gold surface sites; The planar aromatic structure facilitates π – π stacking and dimer formation, promoting adsorption; Adsorption perturbs the local refractive index around AuNPs, altering SPR behaviour.

4. Conclusion

Gold nanoparticles synthesized via the Turkevich method demonstrate strong, stable SPR absorption, confirming the formation of monodisperse spherical AuNPs. Dye–nanoparticle interaction studies showed that sodium fluorescein exhibits strong pH-dependent interaction, especially at alkaline pH (pH 9.2), where dye molecules dimerize and adsorb onto the AuNP surface. This result highlights the critical role of molecular charge, structure, and solution chemistry in determining dye–nanoparticle interactions. The findings have important implications for the design of nano sensors, photocatalysts, and pH-responsive nanomaterials.

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References:

- [1] P. Milan and Alexander H, Nanotechnology: Exploring the Fashion of Thinking Small, 2007.
- [2] K.E. Drexler, Molecular engineering: An approach to the development of general capabilities for molecular manipulation. *Proc Natl Acad. Sci. USA*, 78, 1981, 5275-5287.
- [3] A.P. Nikalje, Nanotechnology and its Applications in Medicine, *Med chem* 5: 081-089, 2015.
- [4] P.T. Bishop, L.J. Ashfield, A. Berzins, A. Boardman, V. Buche, J. Cookson, R.J. Gordon, C. Salcianu, and P.A. Sutton, Printed gold for electronic applications, *Gold Bull.*, 43: 181, 2010.
- [5] W. Göpel, Bioelectronics and nanotechnologies Biosensors and Bioelectronics, 13, 723, 1998.
- [6] K. Wagers, T. Chui, and S. Adem; Effect of pH on the Stability of Gold Nanoparticles and Their Application for Melamine Detection in Infant Formula; *IOSR-JAC*; 7, Issue 8 Ver. II, 1520, 2014.
- [7] C. D. Xiao and S. F. Sui, Characterization of Surface Plasmon Resonance Biosensor, *SENS ACTU-B*, Vol. 66 No. 1-3, pp. 174-177, 2000.
- [8] J. Zhao, X. Zhang, C.R. Yonzon, A.J. Haes, and R. P. Vanduyne, Localised Surface Plasmon Resonance Biosensors, *Nanomedicine*, Vol. 1, No. 2, pp. 219-228, 2006.
- [9] J. Turkevich, P.C. Stevenson and J. Hillier: A study of the nucleation and growth process in the synthesis of colloidal gold. *Discuss. Faraday Soc.*, 11, 55-75, 1951.
- [10] V. Sonia, R. S. Sindala, and R. N. Mehrotra, *Inorg. Chim. Acta*, 360, 3141, 2007.
- [11] X. Wu; P. L. Redmond, H. Liu, Y. Chen, M. Steigerwald, and L. J. Brus, *Am. Chem. Soc.*, 130, 9500, 2008.
- [12] T. John Hewitt and B. W. Perkins, *Journal of the Chemical Society, Transactions*, 77, 1324-1334, 1990.
- [13] L. A. Dykman and N. G. Khlebstov, Gold Nanoparticles in biology and medicine: Recent Advances and Prospectus, *Acta Naturae*, Volume 3, No.2 (9), 3455, 2011.
- [14] R.A. Moses; Fluorescein in applanation tonometry, *Am. J. Ophthalmol.*, 1149-55, 1960.
- [15] A. Cook and A. Le, The effect of solvent and pH on the fluorescence excitation and emission spectra of solution containing fluorescein, *J. Phys. Chem. Lab*, 10, 44-49, 2006.
- [16] J. Panchompoo, L. Aldous, M. Baker, and R.G. Comptom, *Analyst*, 137, 2054, 2012.
- [17] R. Sjöback, J. Nygren, and M. Kubista, *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, 51(6), L7-L21, 1995.
- [18] S. Sukprasong and A. Ngamjarurojana, Dimer formation effect on red-shift in fluorescent spectra of dye solutions, *Proceedings SPIE 9659, International Conference on Photonics Solutions*, 96590 G, 2015.
- [19] G. Su, S. Yin, L. Wan, J. Zhao, and C. Bai, Dimerisation of three xanthene dyes on Au (111) surface, *Surface Chemistry*, Volume 551, Issue 3, 204-212, 2004.
- [20] H. Kitching; A.J. Kenyon and I.P. Parkin, The interaction of gold and silver nanoparticles with a range of anionic and cationic dyes, *Physical Chemistry Chemical Physics*, 16, 6050-6059, 2014.
- [21] G. Dutta, S. Paul, M. Bardhan, and T. Ganguly, Interactions of fluorescein dye with spherical and star-shaped gold nanoparticles, *Journal of nanoscience and nanotechnology*, Vol.18, 2943-2950, 2018.