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Electronic supplementary information

A rapid and sensitive colorimetric discrimination and detection of cysteine, homocysteine and glutathione by Phloroglucinol functionalized silver nanoresonators with real applications

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New Journal of Chemistry

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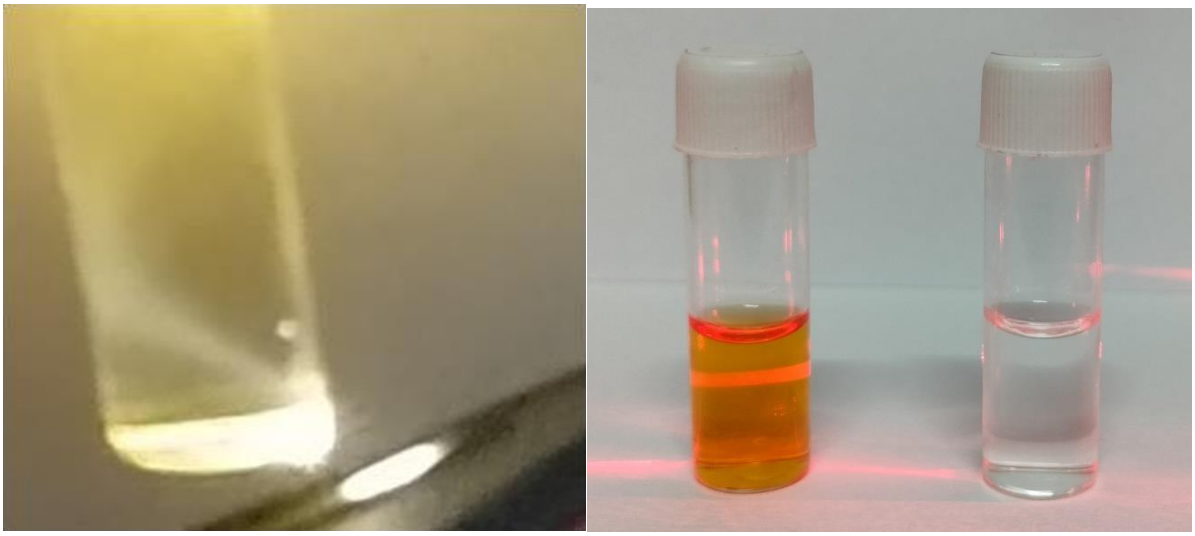


(a) **(b)**

Fig.S1: Image showing Tyndall effect.

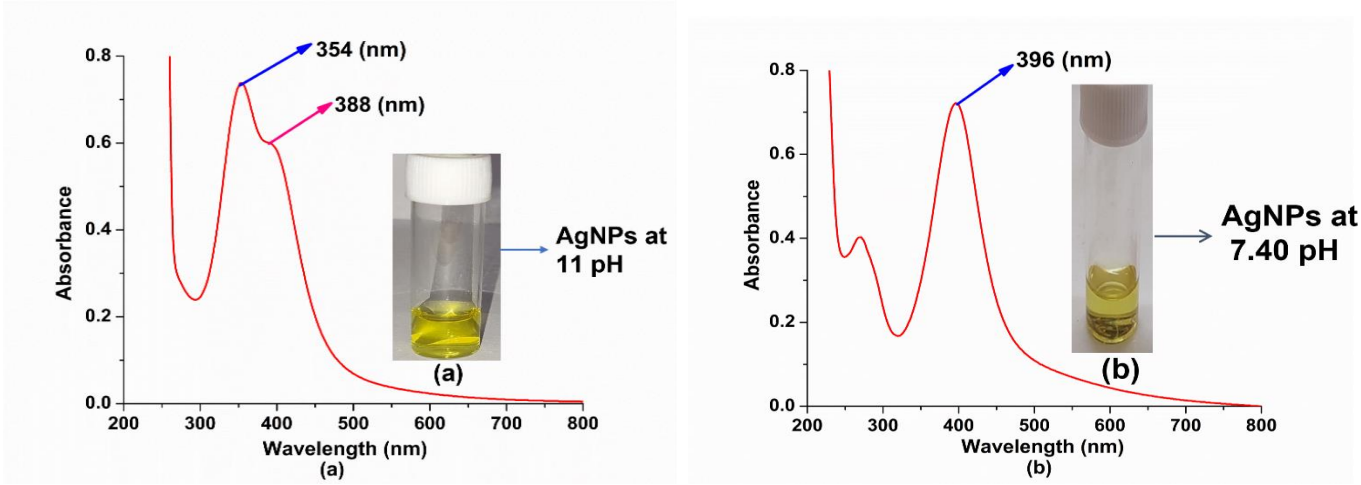


Fig.S2: Image showing the color and UV-Vis spectral patterns (a) at pH 11.00 (b) at pH 7.40.

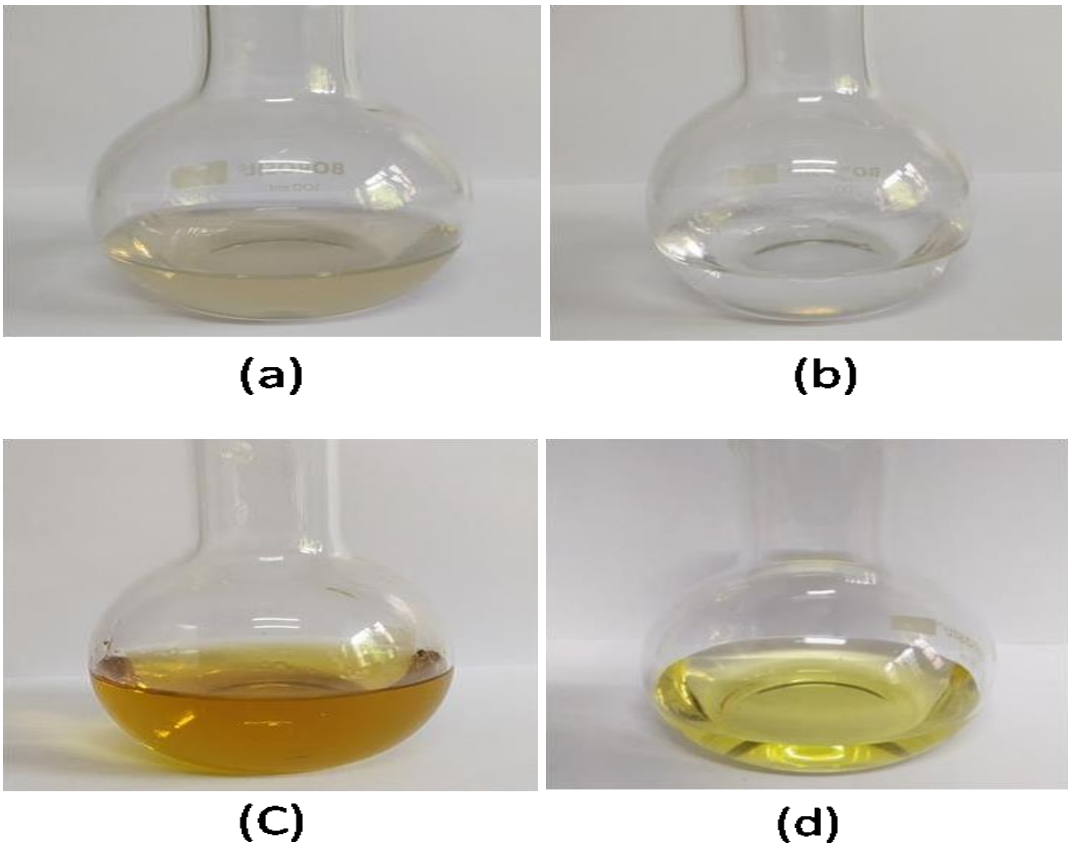


Fig.S3: Image showing various solution (a) $AgNO_3$+NaOH (without Phloroglucinol) (b)$AgNO_3$+Phloroglucinol (without NaOH) (c) silver nanoparticles at ≈ 11pH (d) silver nanoparticles at 7.40 pH.

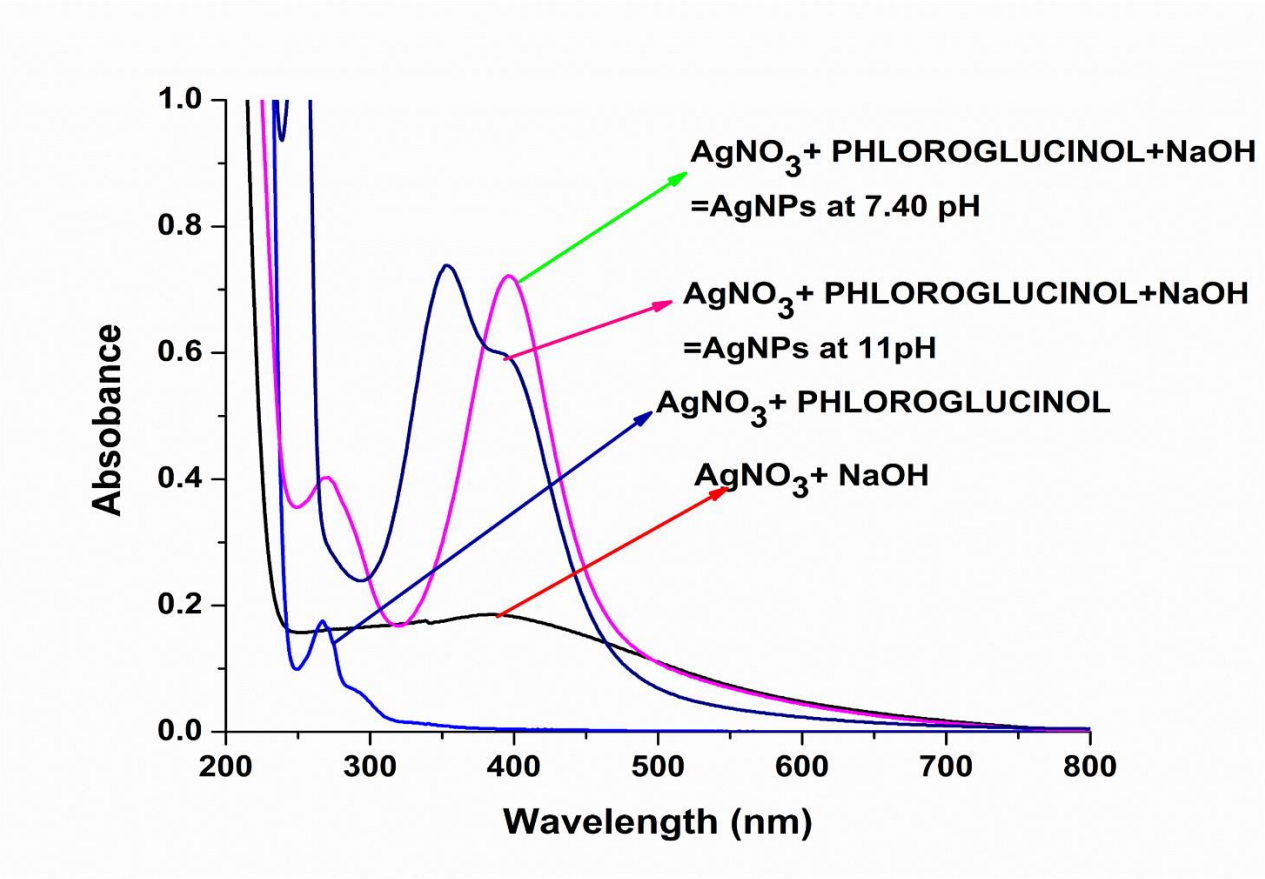


Fig.S4: UV-Visible spectra of various controlled preparations and AgNPs preparations (pH 11and pH 7.4).

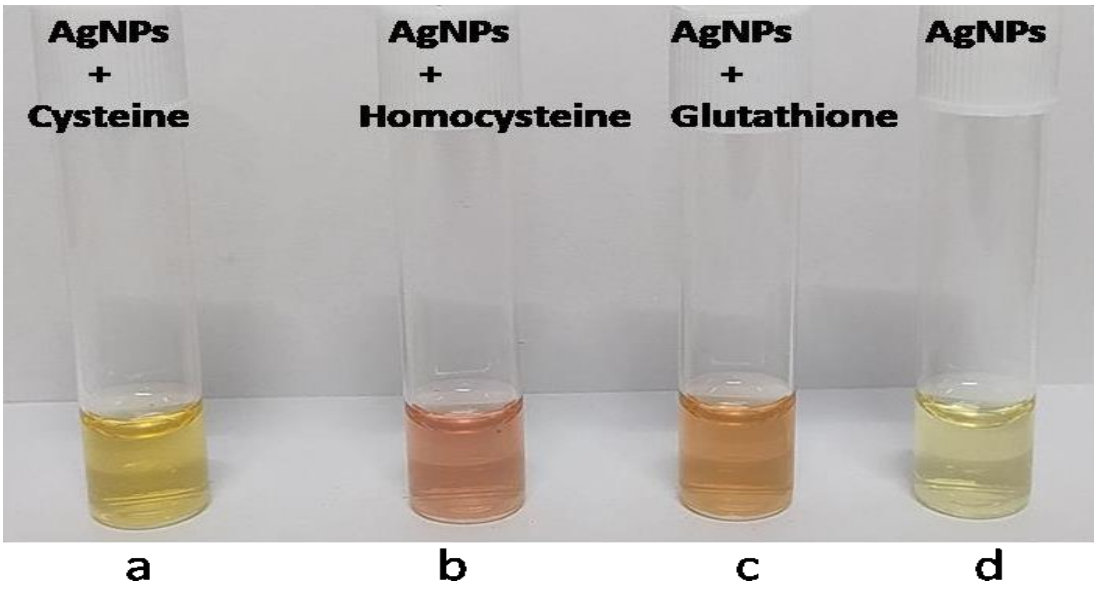


Fig.S5: Showing visual responses:(a) AgNPs with Cysteine (b) AgNPs with Homocysteine (c) AgNPs with Glutathione(d) AgNPs at pH 7.4

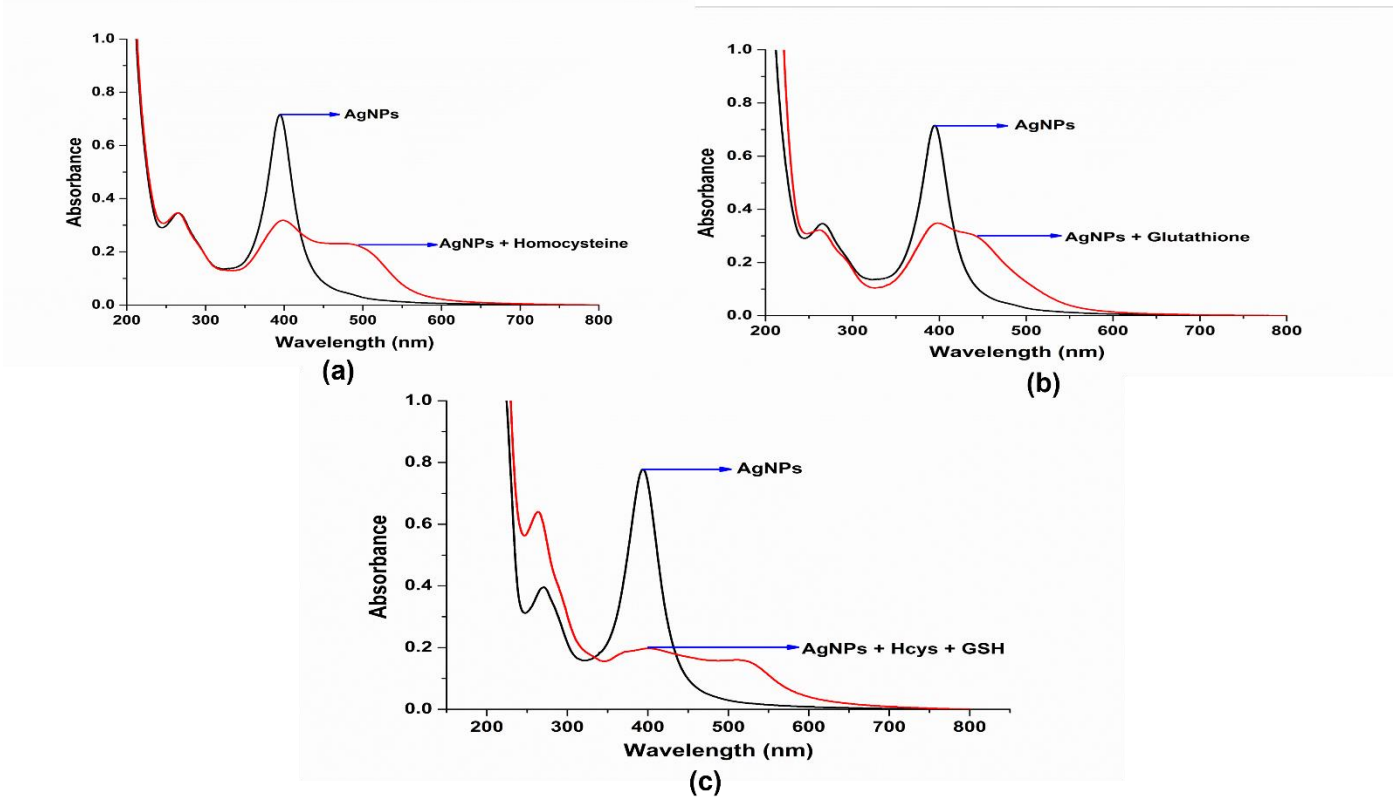
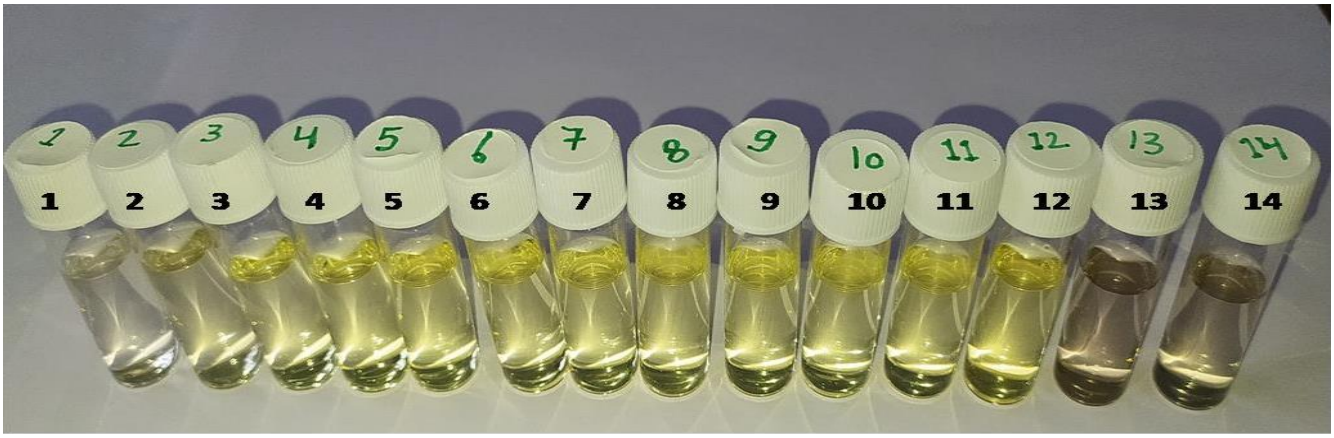


Fig.S6: UV-Vis spectral responses (a) AgNPs before and after addition of homocysteine (b) AgNPs before and after addition of Glutathione (c) AgNPs before and after addition of mixture of Homocysteine and Glutathione (1:1).



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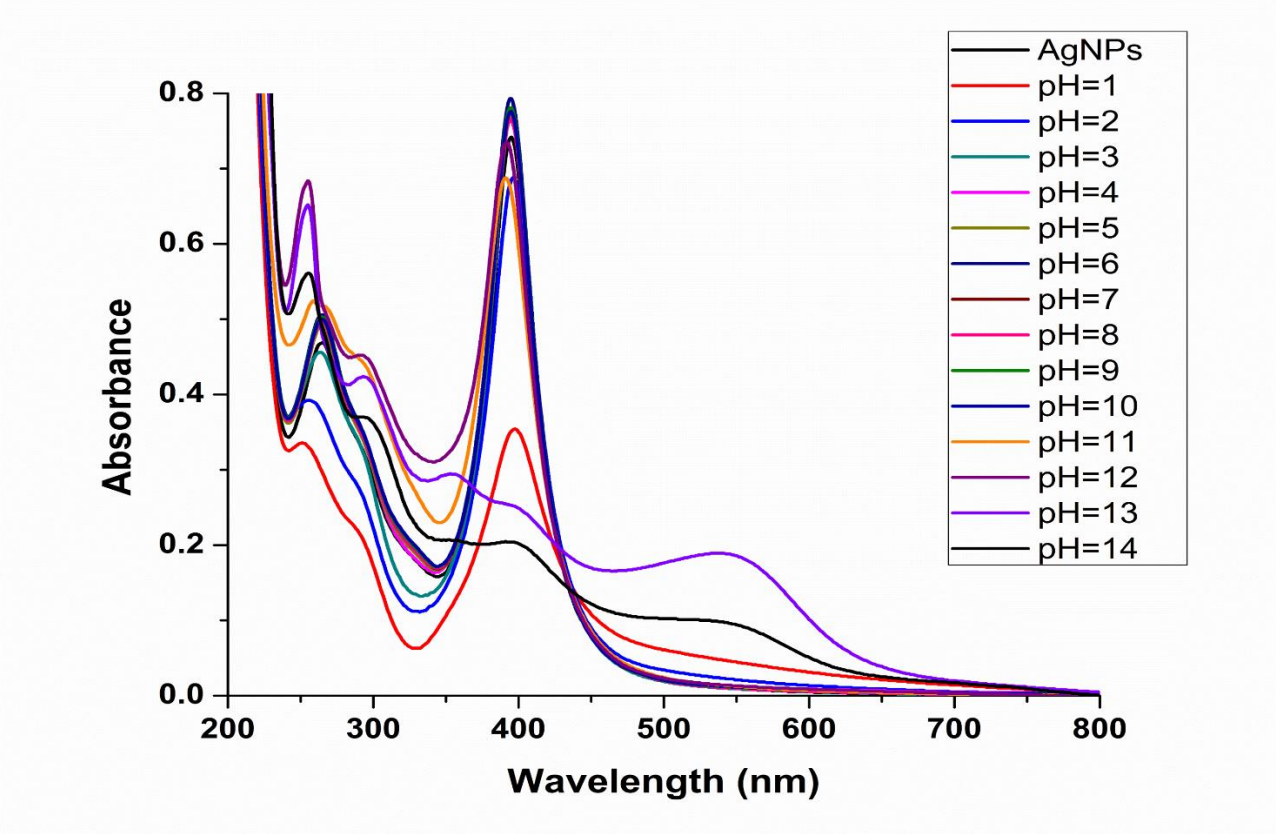
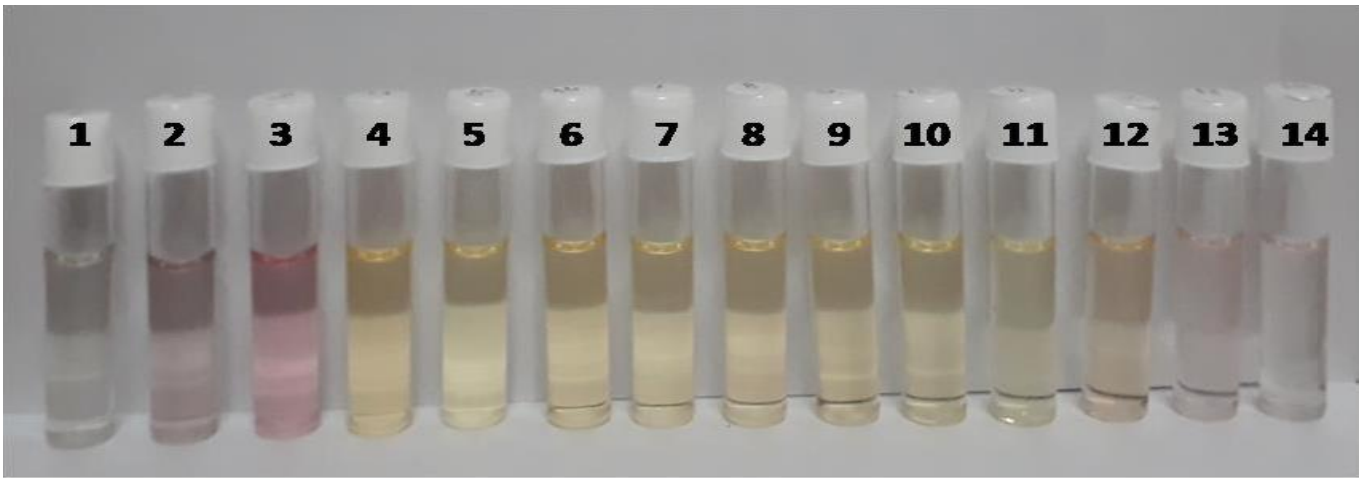


Fig.S7:(a) Visual and (b) UV-Visible spectral responses of AgNPs with respect to variation of pH (1-14).



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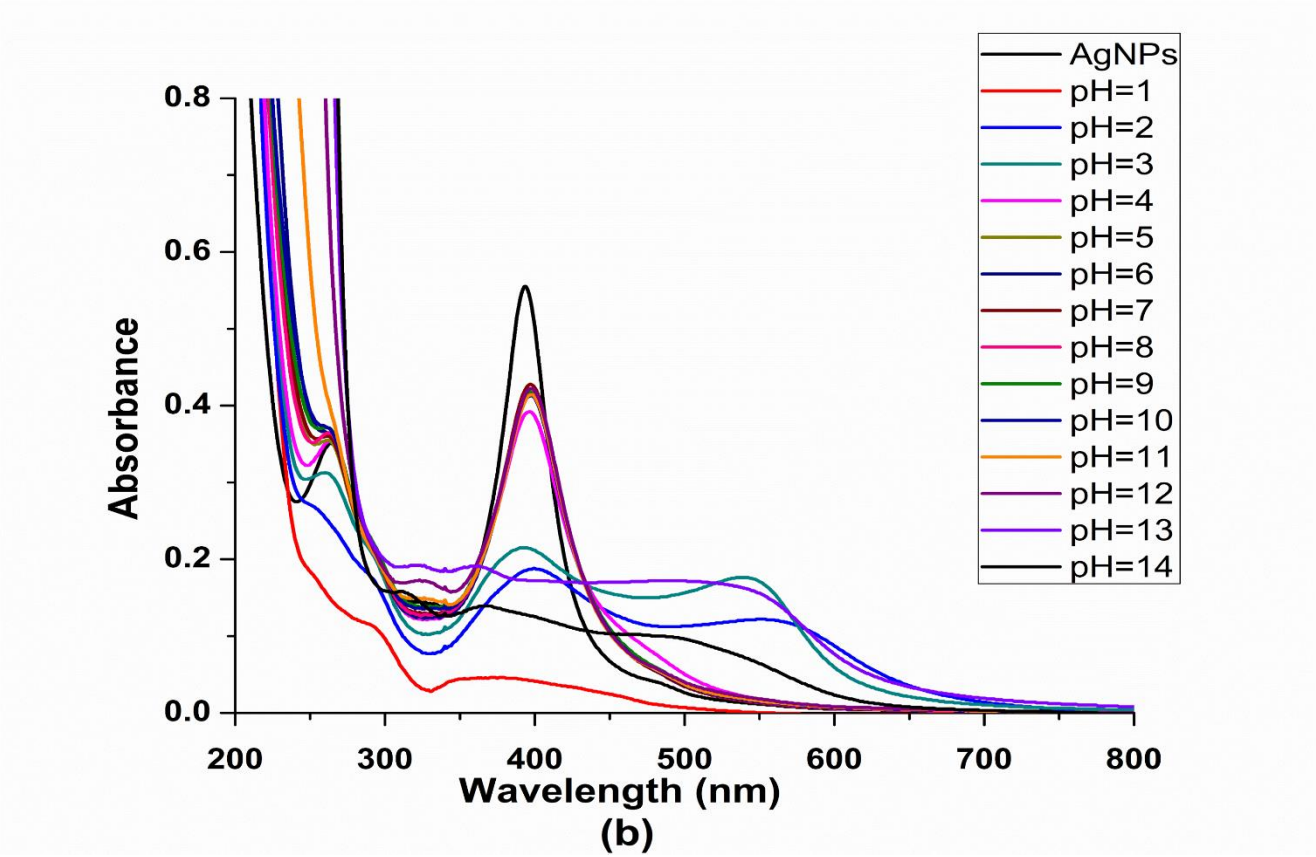
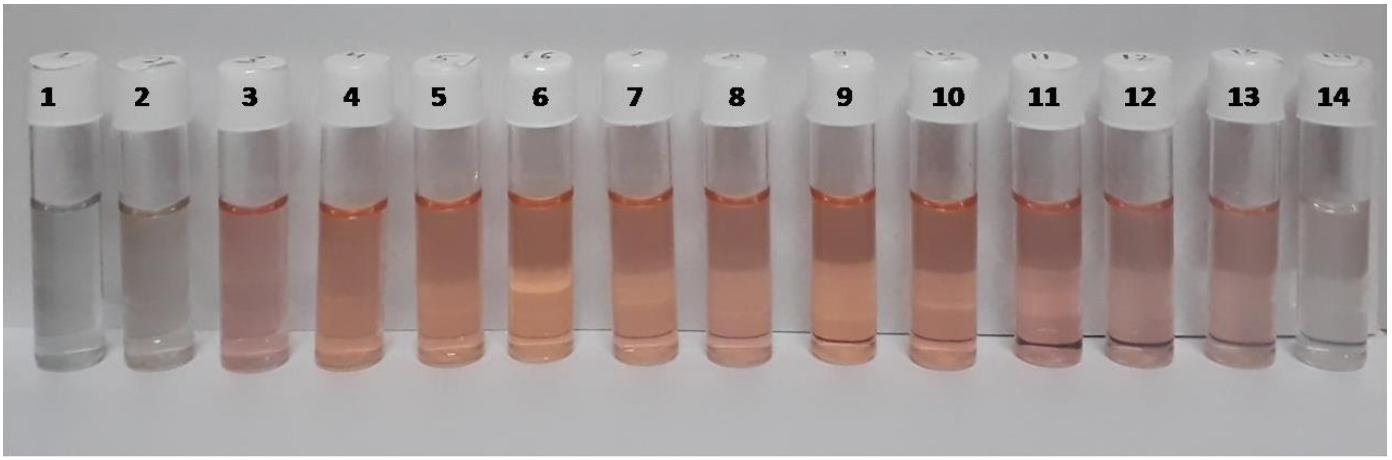


(b)

Fig.S8: (a) Visual (b) UV-Visible spectral responses for the interaction of Cysteine with AgNPs with respect to variation of pH (1-14).



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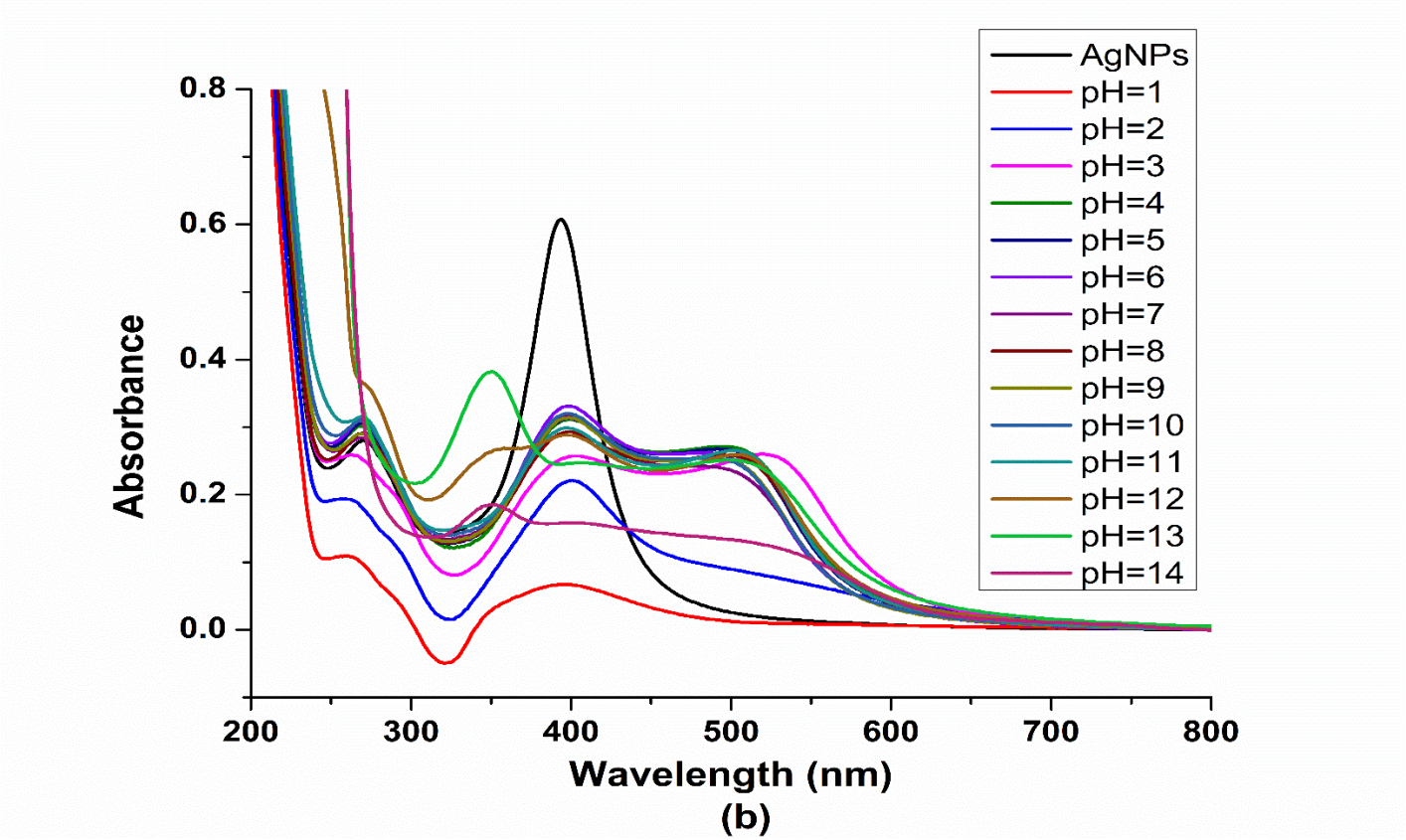
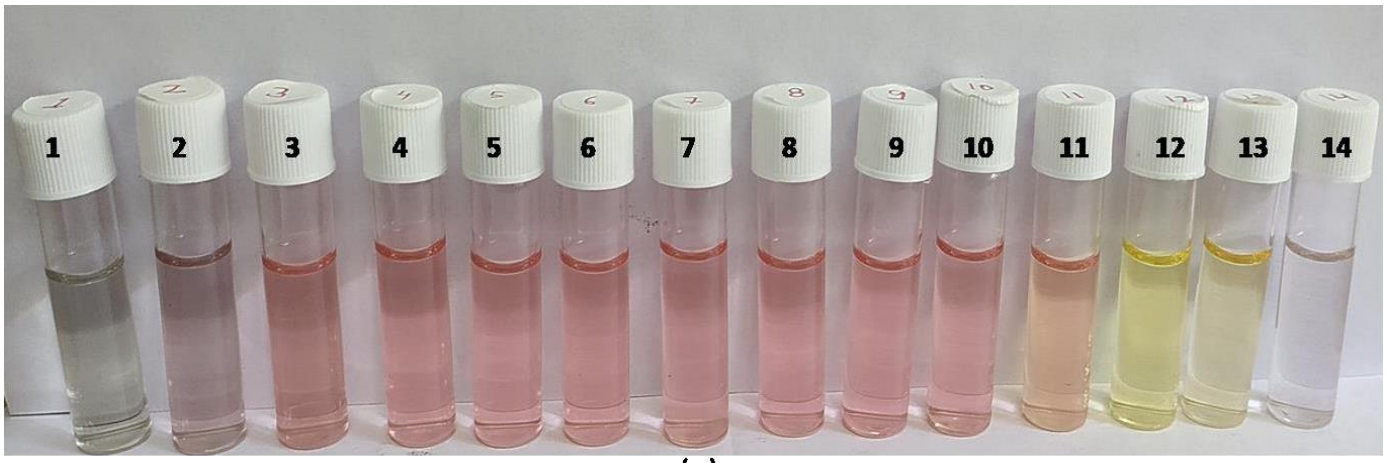


(b)

Fig.S9: pH study after addition of Homocysteine (a) Visual response of AgNPs after addition of Homocysteine in the pH range (1-14). (b) UV-Visible spectra of corresponding AgNPs after addition of Homocysteine in the pH range (1-14).



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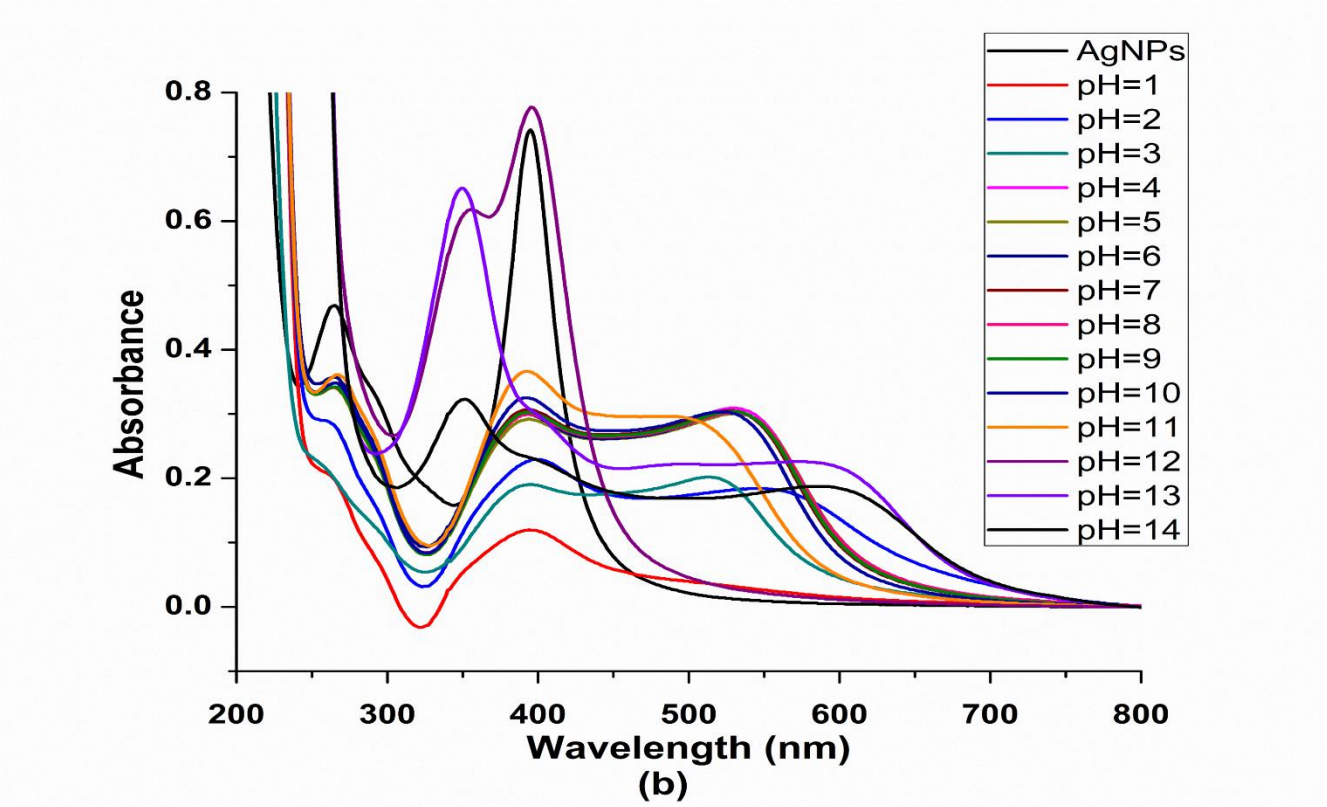


(b)

Fig.S10: pH study after addition of Glutathione (a) Visual response of AgNPs after addition of Glutathione in the pH range (1-14). (b) UV-Visible spectra of corresponding AgNPs after addition of Glutathione in the pH range (1-14).

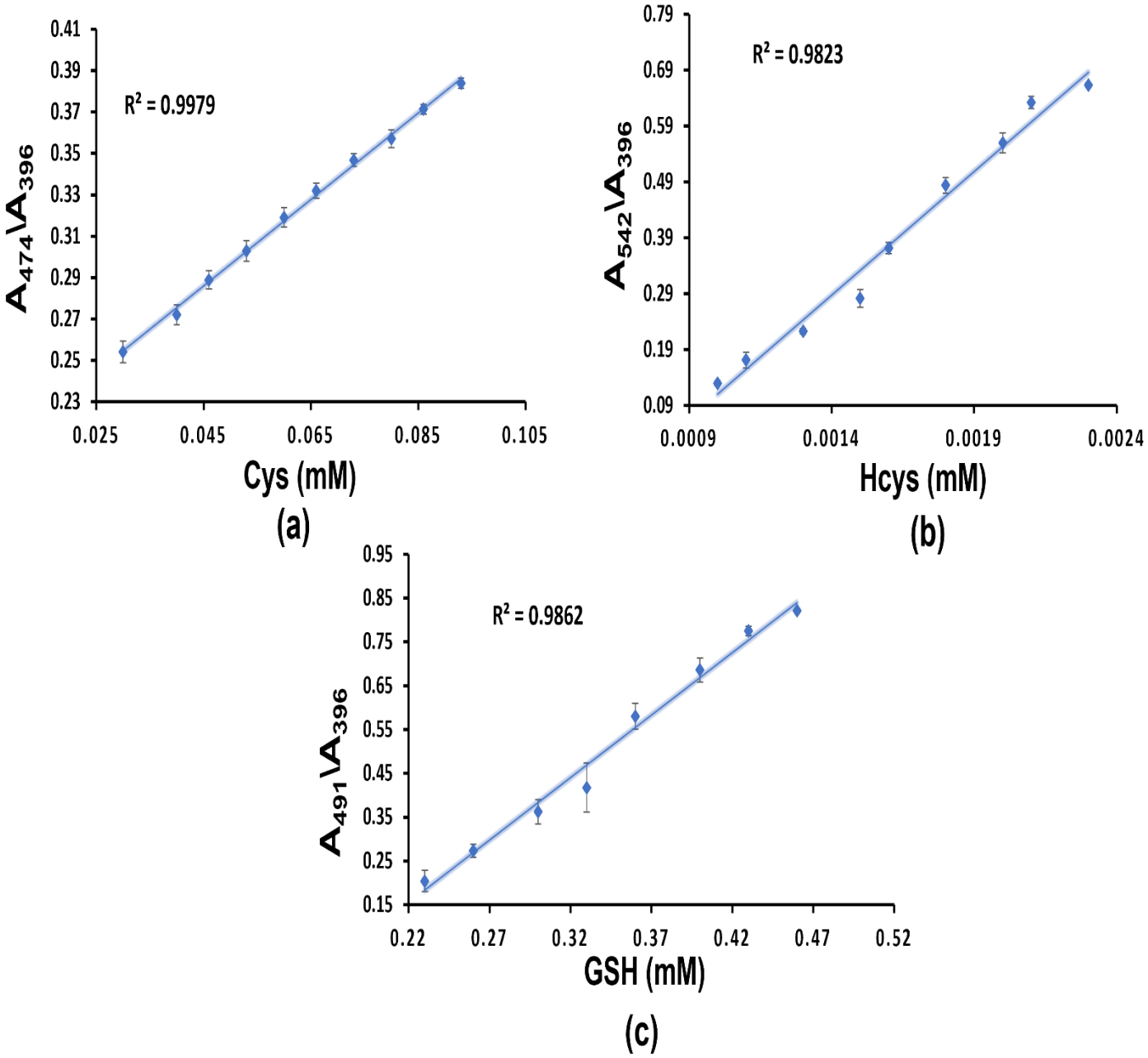
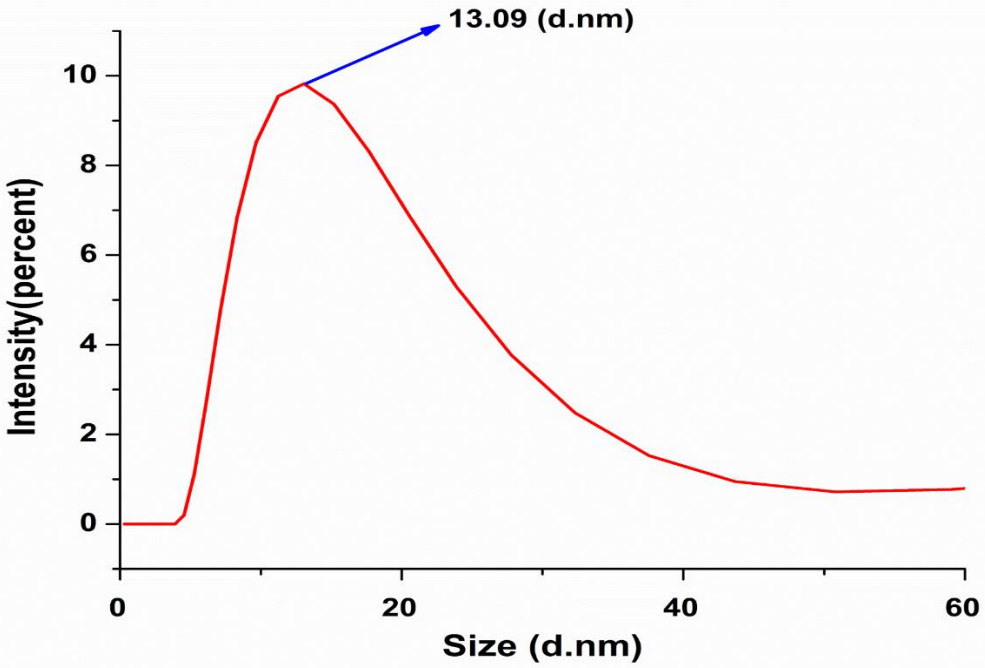


Fig.S11: Calibration plots for chosen analytes with corresponding LOD and linearity range: (a) Cysteine (4.1, µM, 0.033-0.093 mM) (b) Homocysteine (0.16 µM, 0.001-0.0023 mM). (c) Glutathione (3.1 µM, 0.23-0.46 mM).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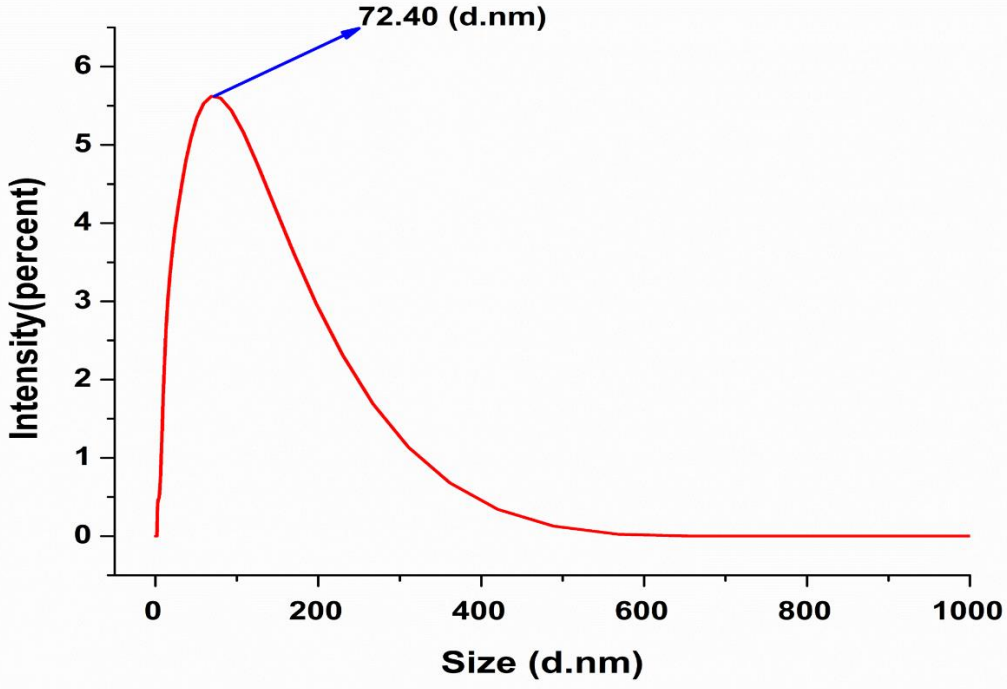
0
20
40
60

(a)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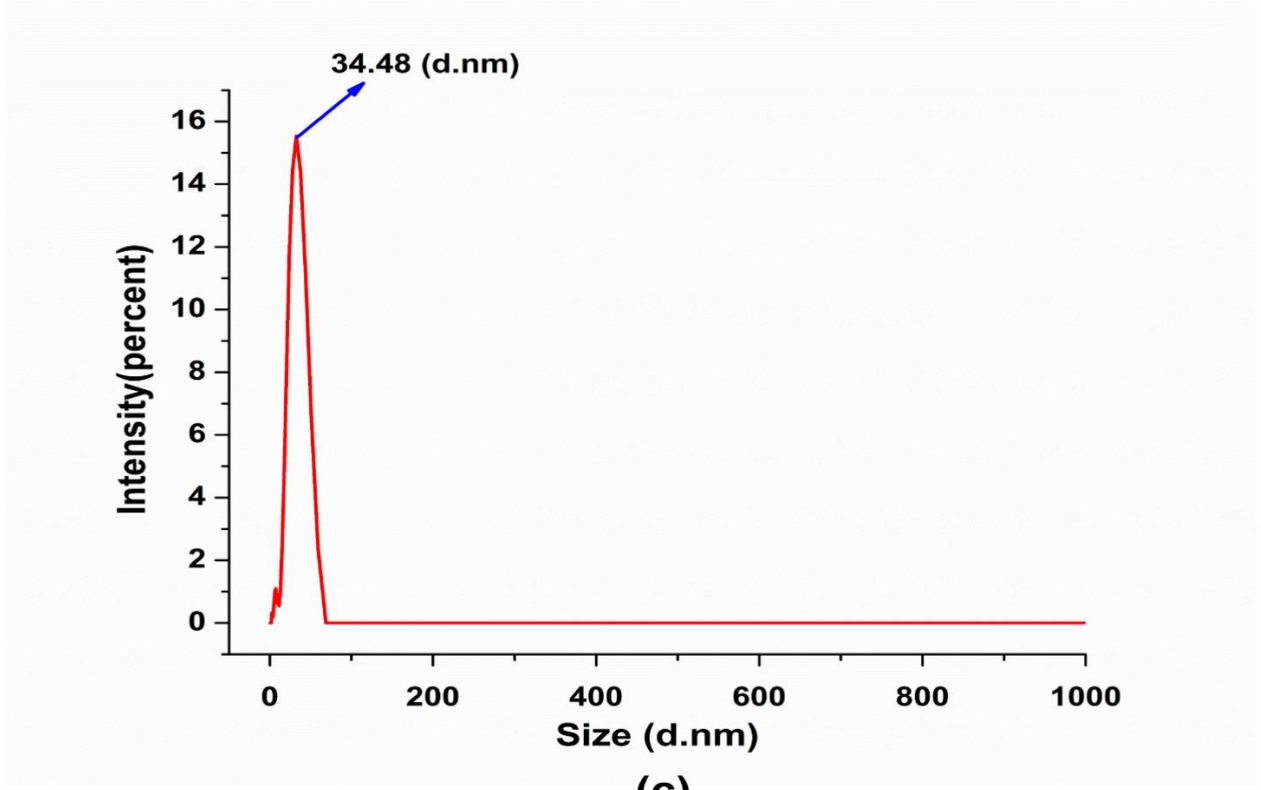
600
800
1000

(b)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12
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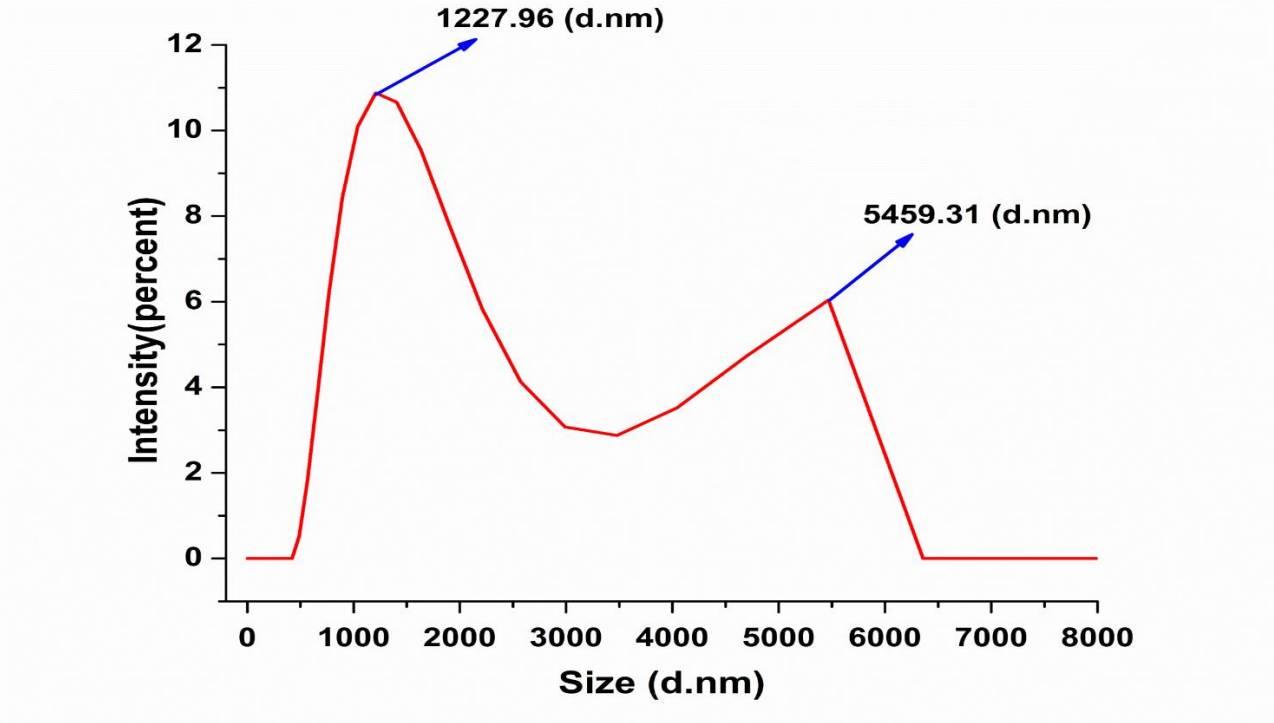
(c)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2000
3000
4000
5000
6000
7000
8000

(d)

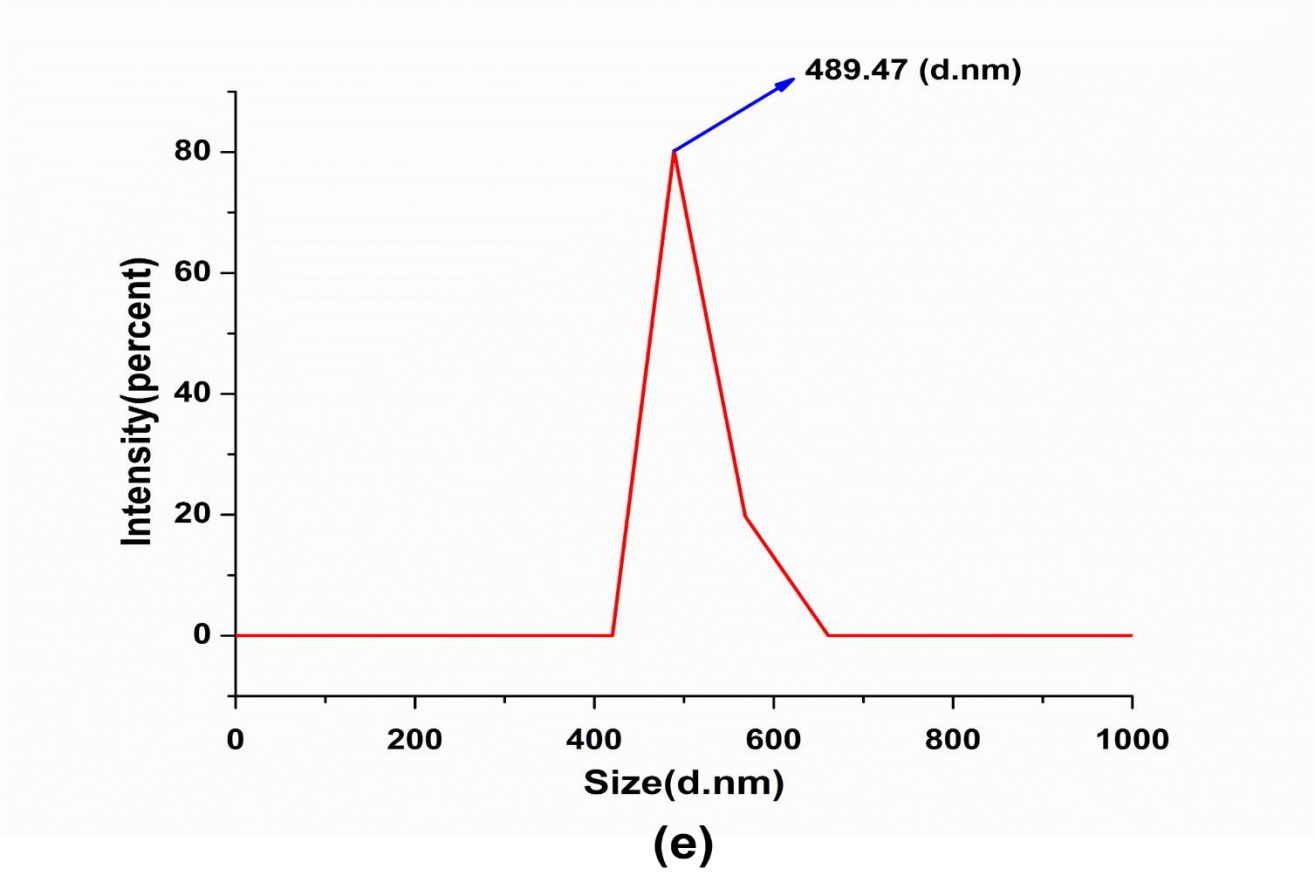
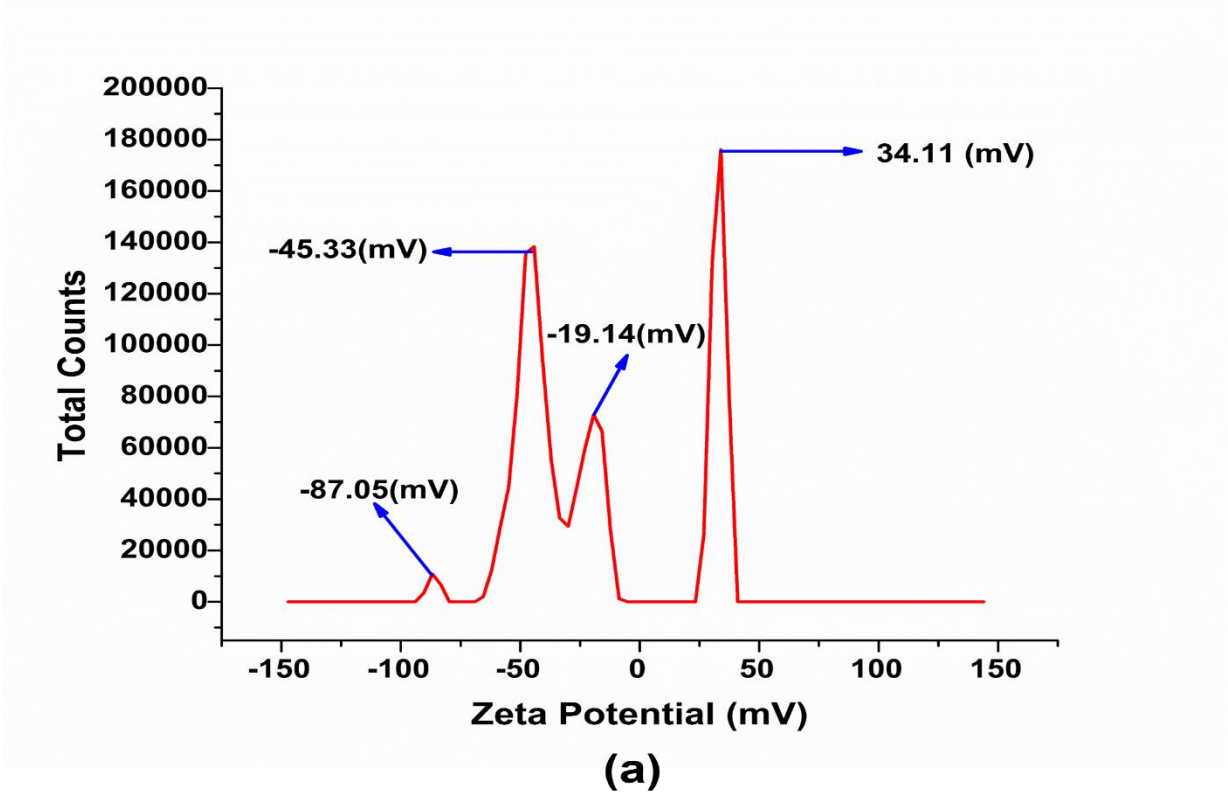


Fig.S12: Dynamic Light Scattering (DLS) Study showing hydrodynamic dimeters of: (a) AgNPs at pH 11. (b)AgNPs at pH 7.40. (c) AgNPs after addition of Cysteine (d) AgNPs after addition of Homocysteine. (e) AgNPs after addition of Glutathione.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120000
100000
80000
60000
40000
20000
0
-150
-100
-50
0
50
100
150
Zeta Potential (mV)
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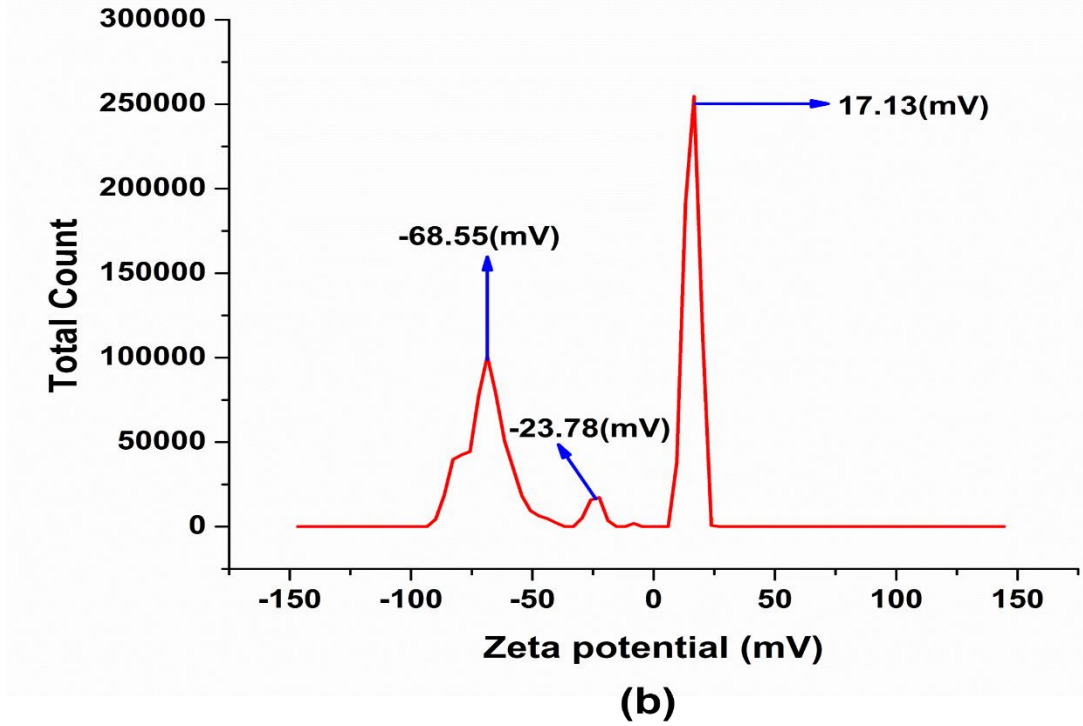
-45.33(mV)
-19.14(mV)
-87.05(mV)

(a)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50
100
150
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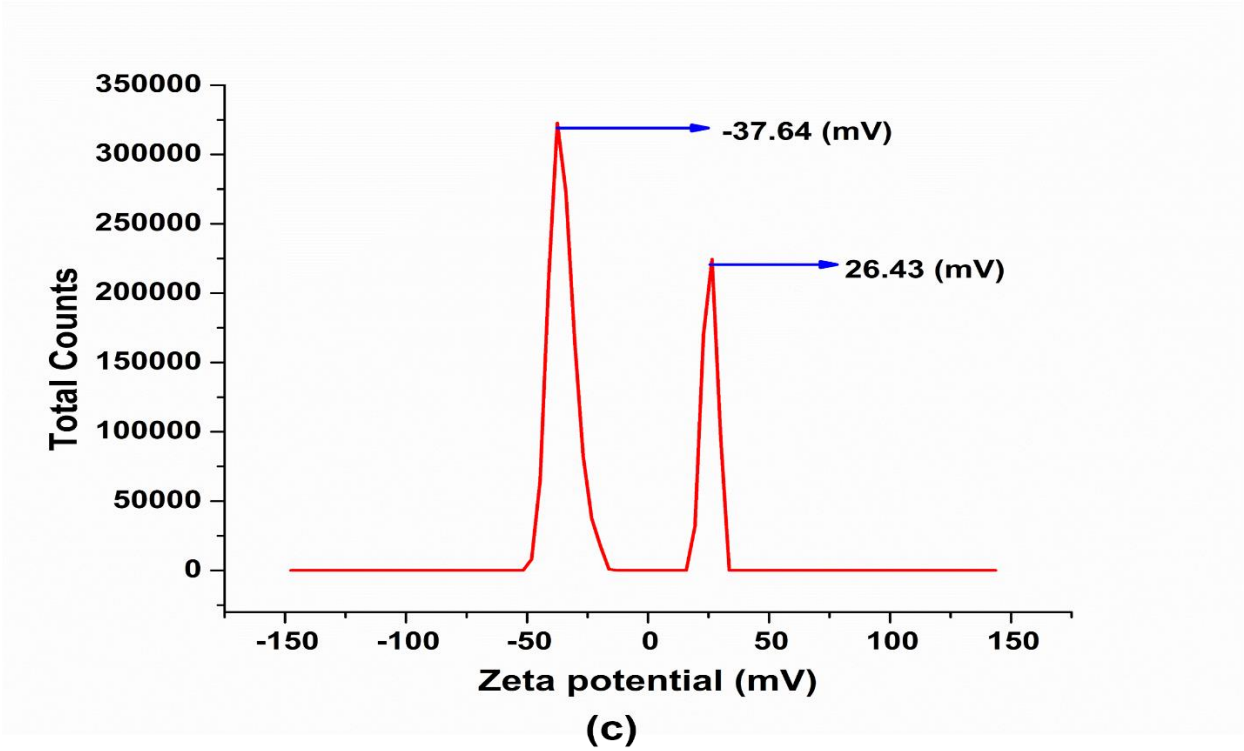
-68.55(mV)
-23.78(mV)

(b)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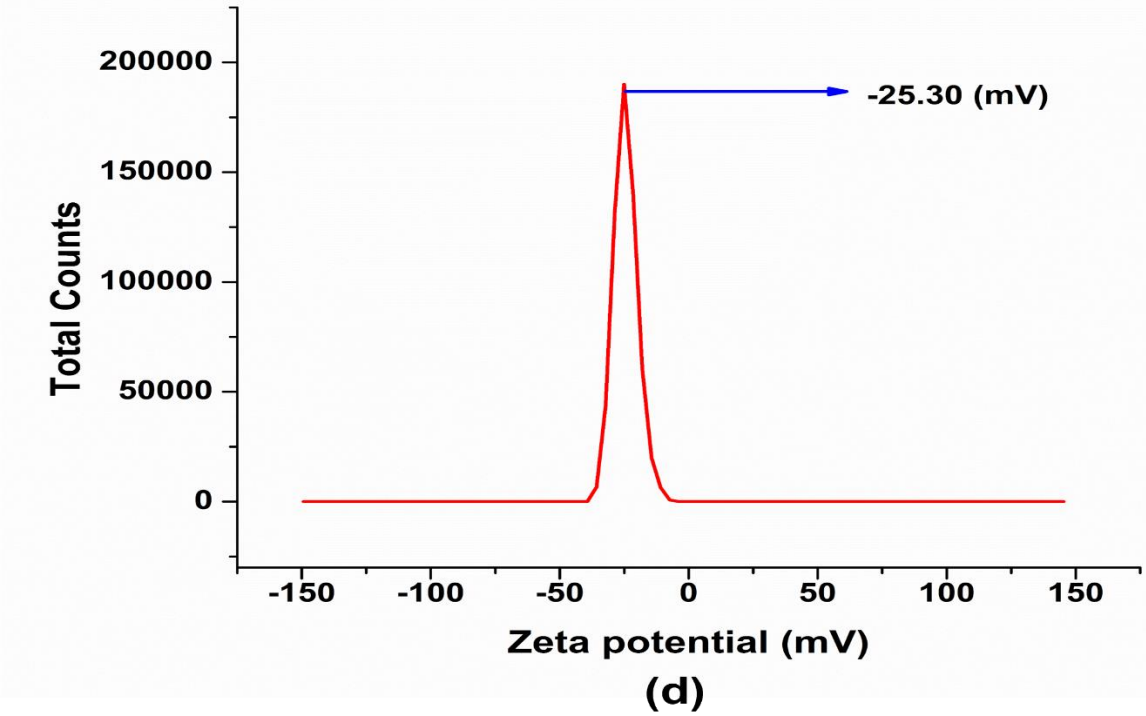
50
100
150
Zeta potential (mV)

(c)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Zeta potential (mV)

(d)

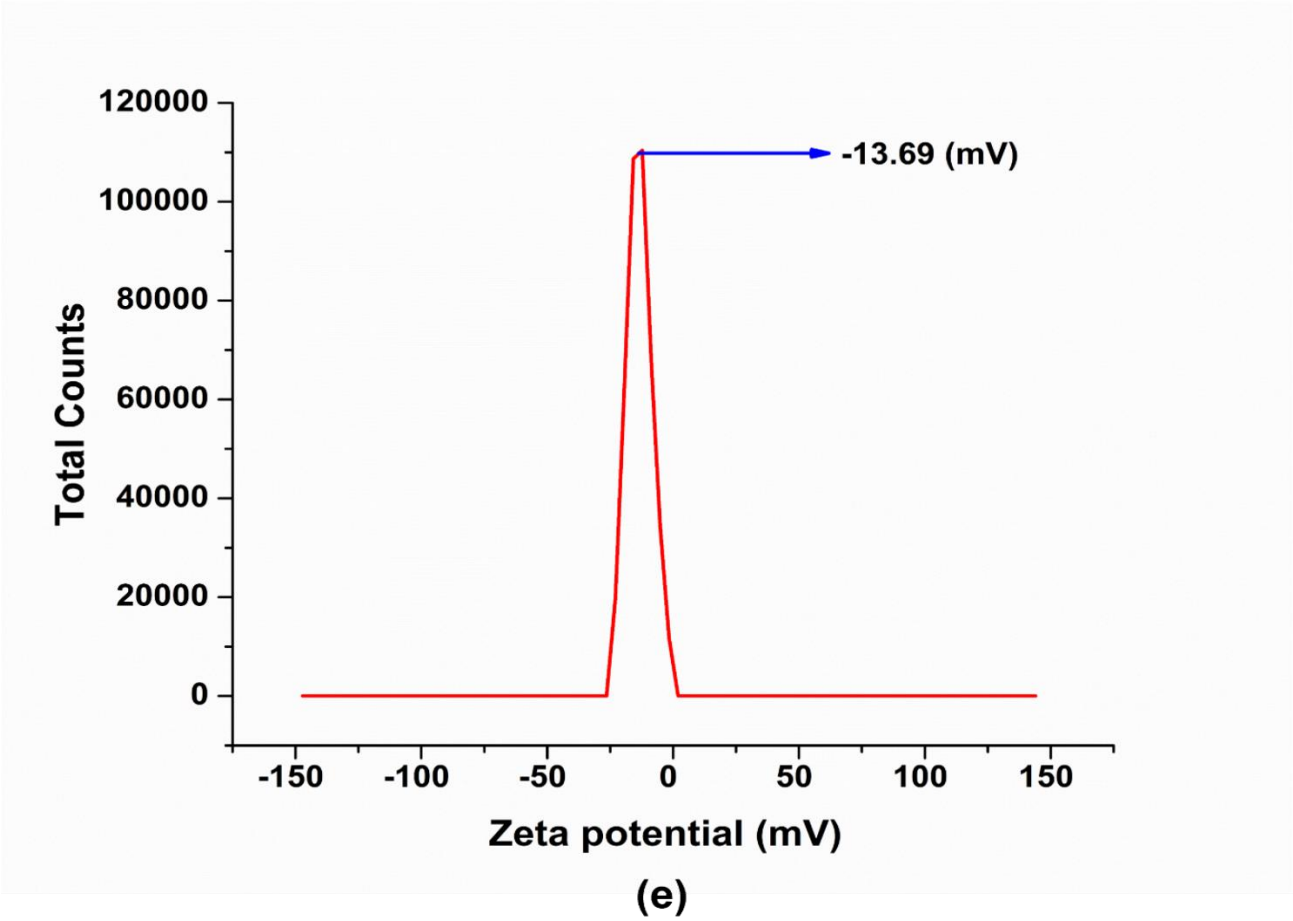
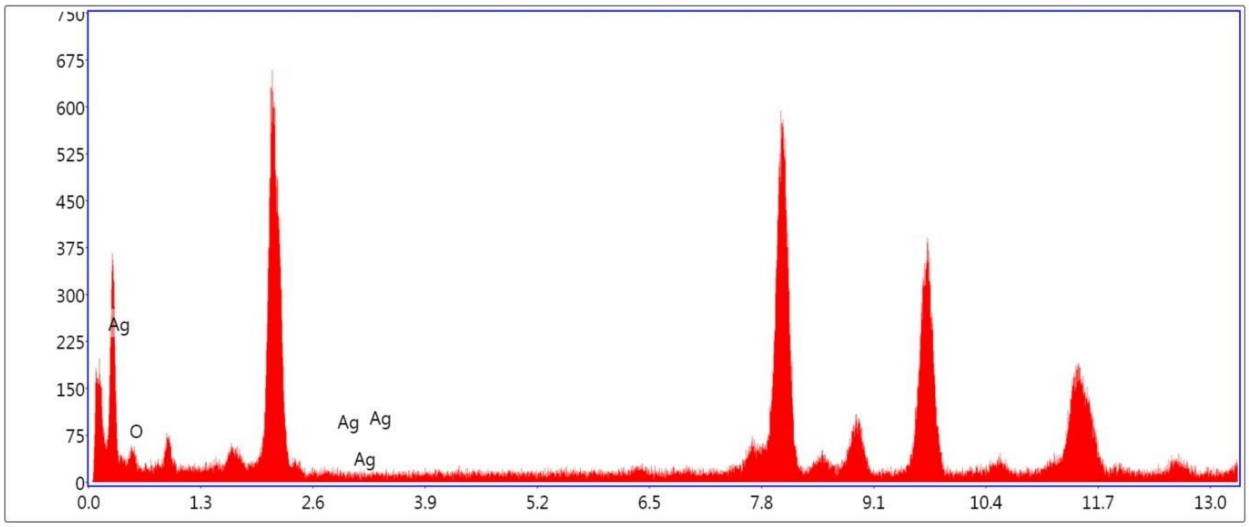


Fig.S13: Evaluations of Zeta Potentials for: (a) AgNPs at pH 11. (b) AgNPs at pH 7.40. (c) AgNPs after addition of Cysteine. (d) AgNPs after addition of Homocysteine. (e) AgNPs after addition of Glutathione.



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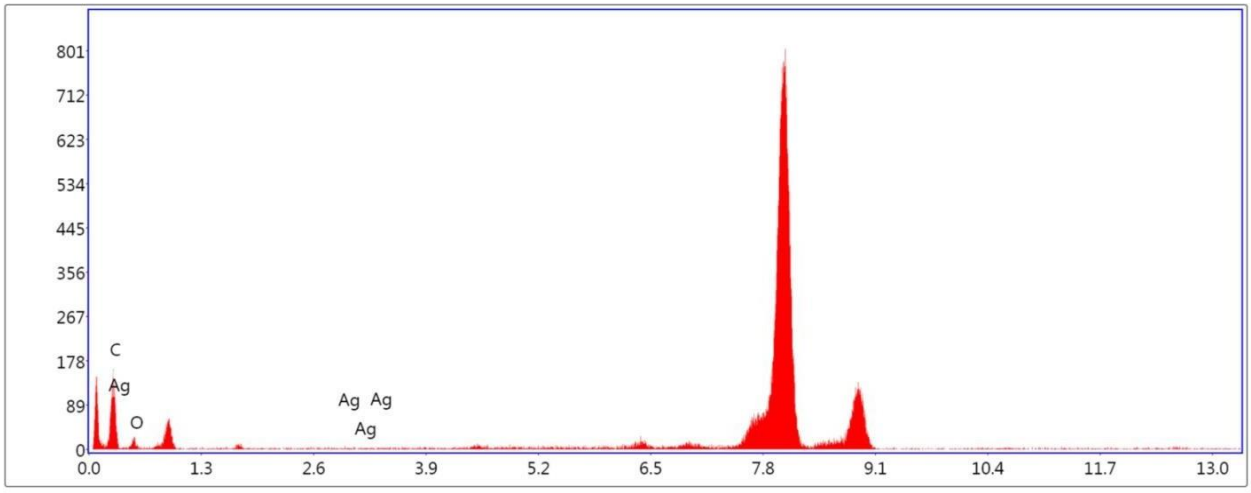

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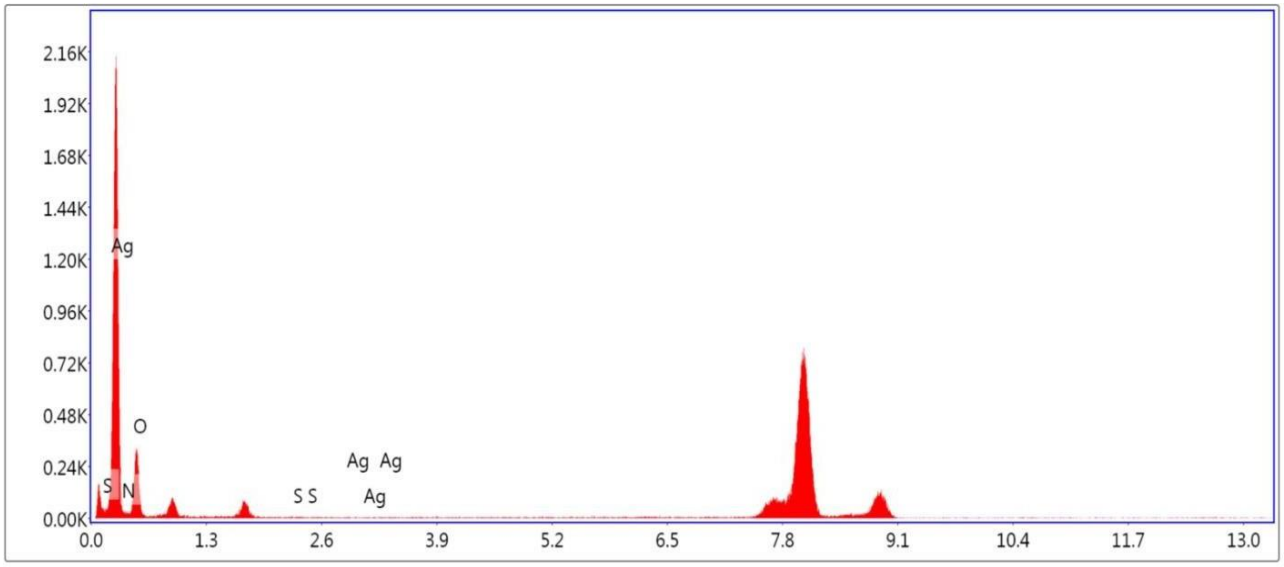

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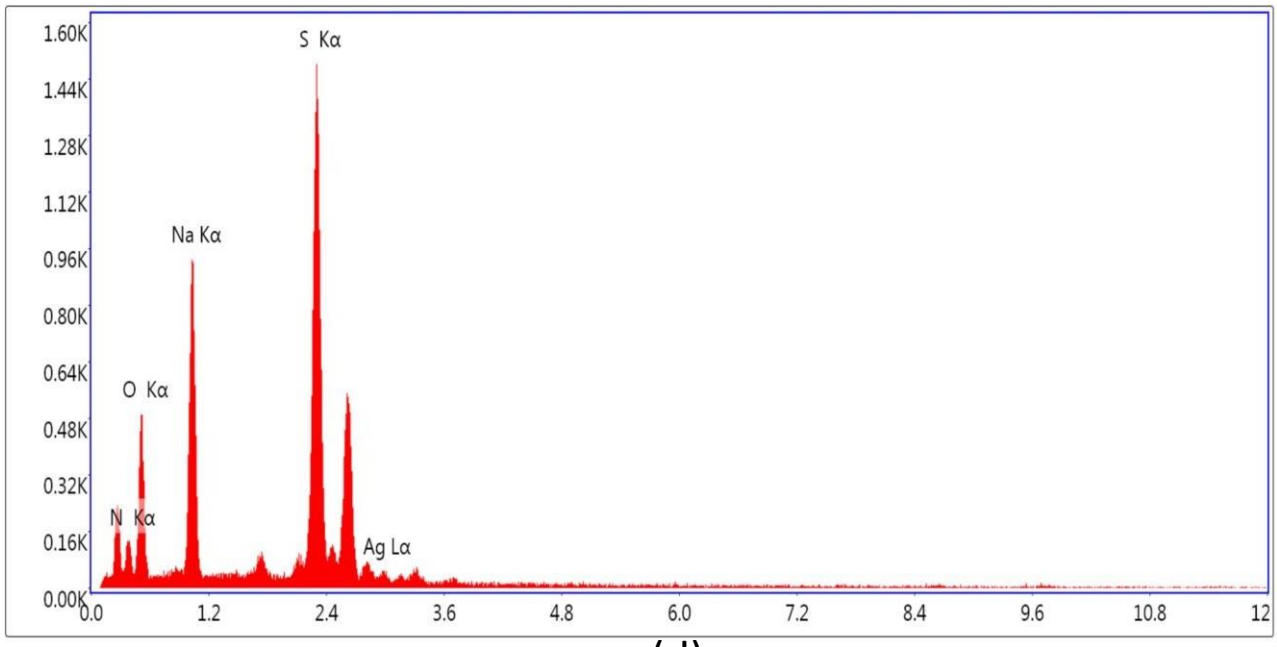

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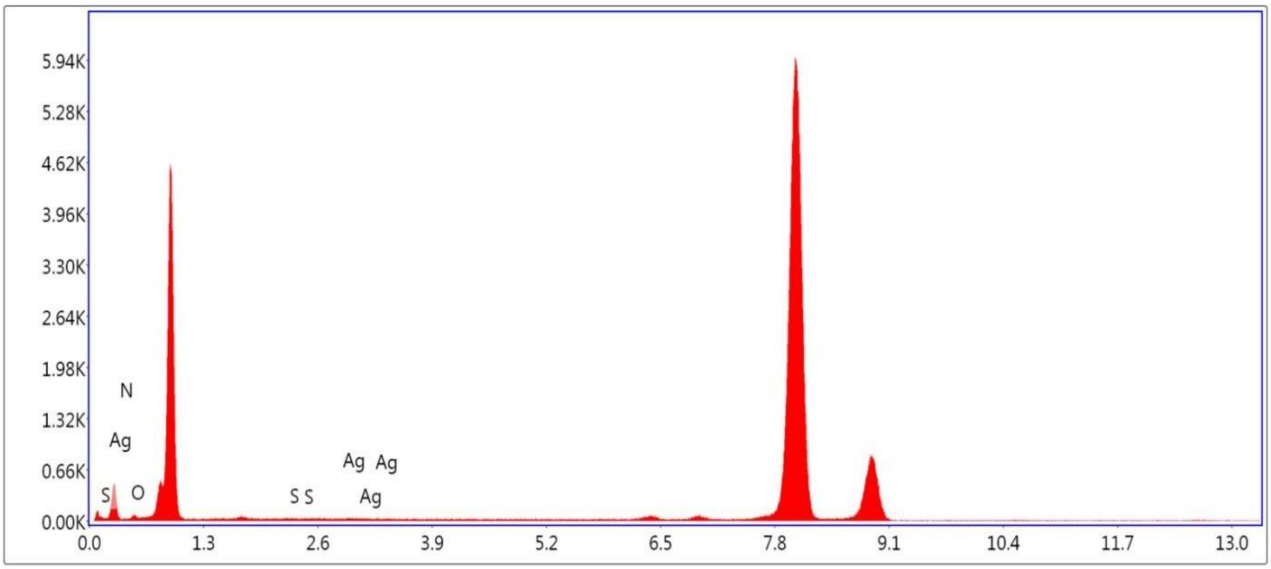
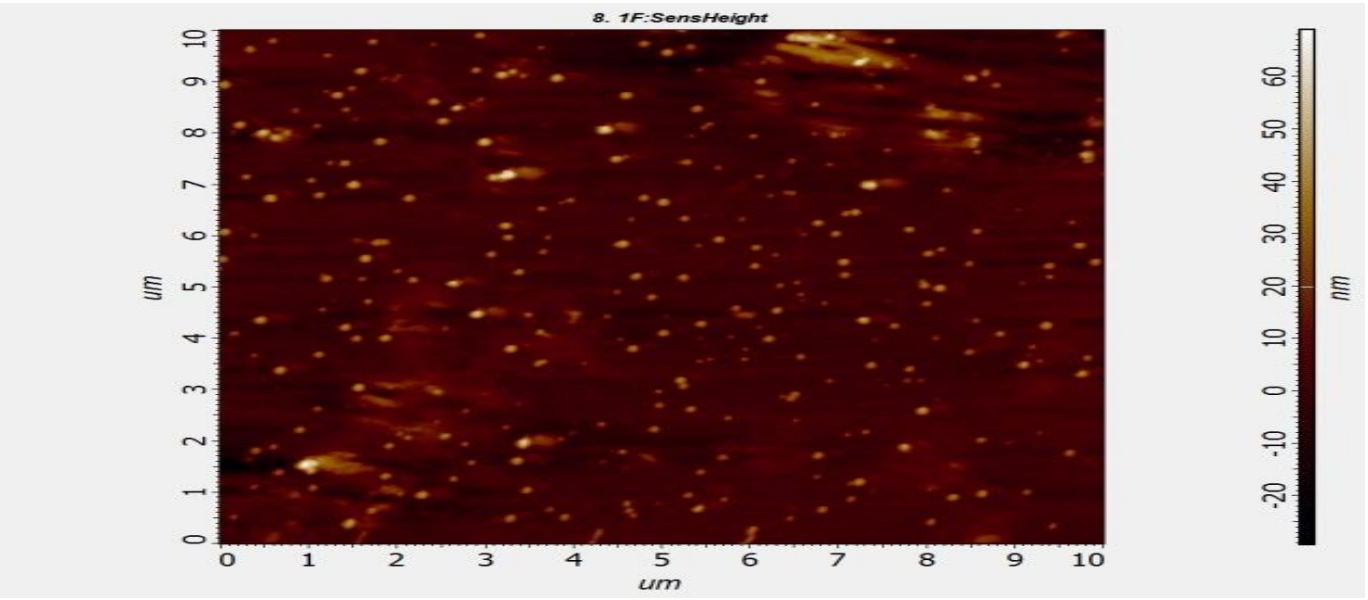


(e)

Fig.S14: Elemental analysis through EDAX: (a) AgNPs at pH 11. (b) AgNPs at pH 7.40.(c) AgNPs after addition of Cysteine. (d) AgNPs after addition of Homocysteine. (e) AgNPs after addition of Glutathione.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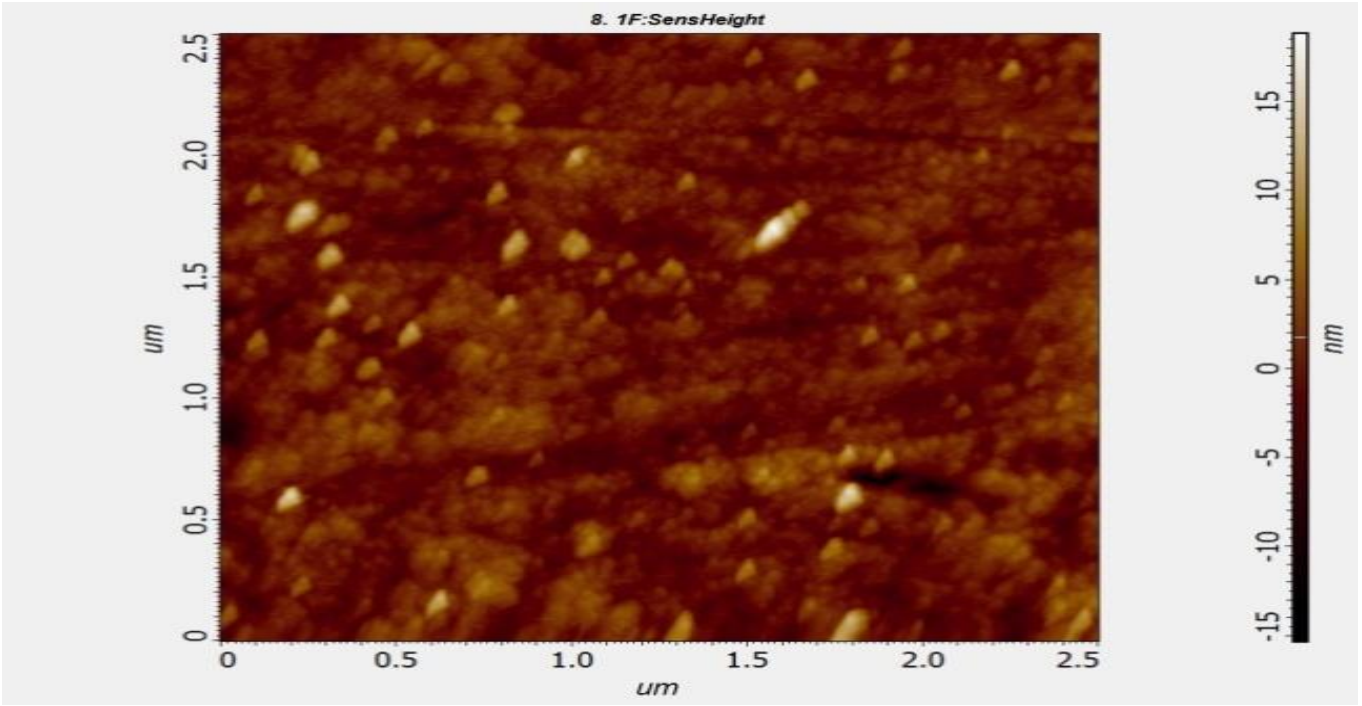
(a)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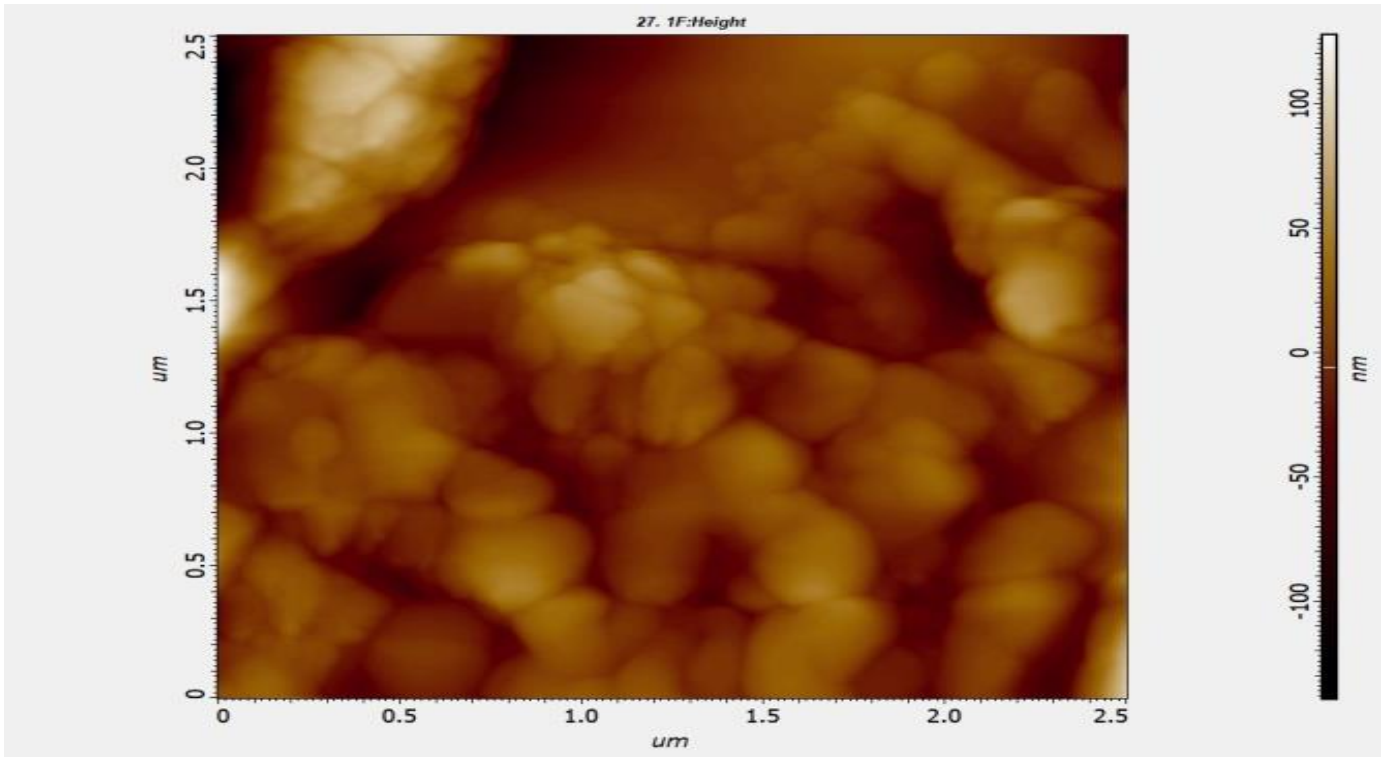
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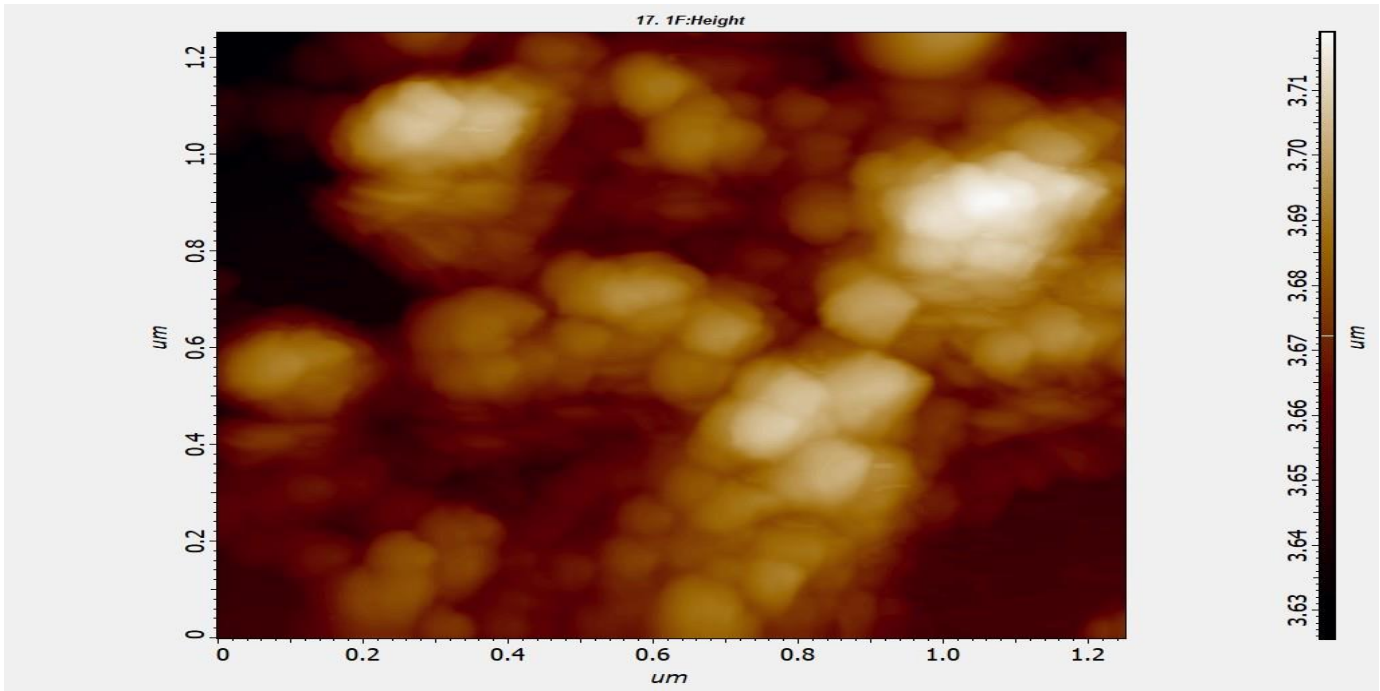
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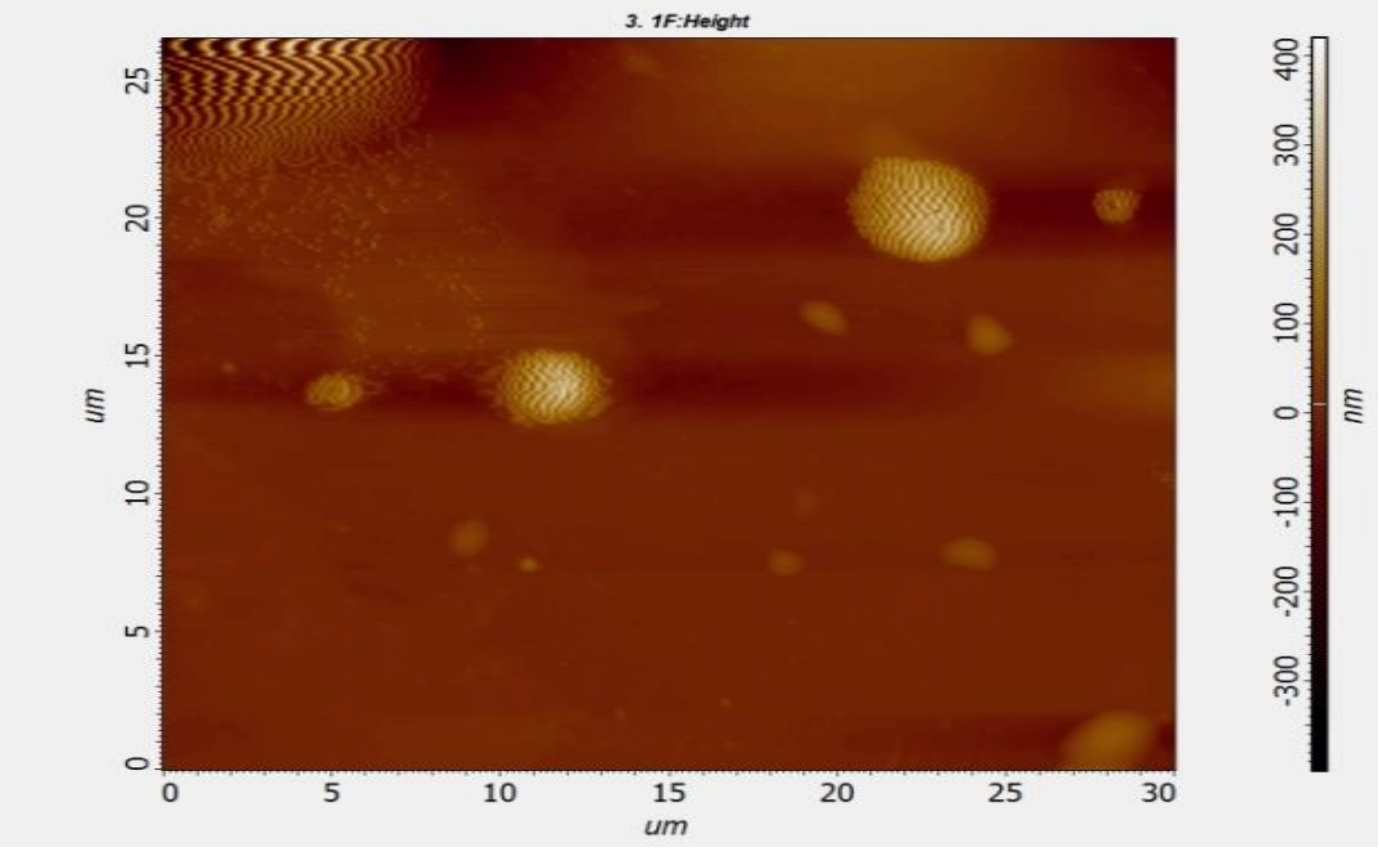
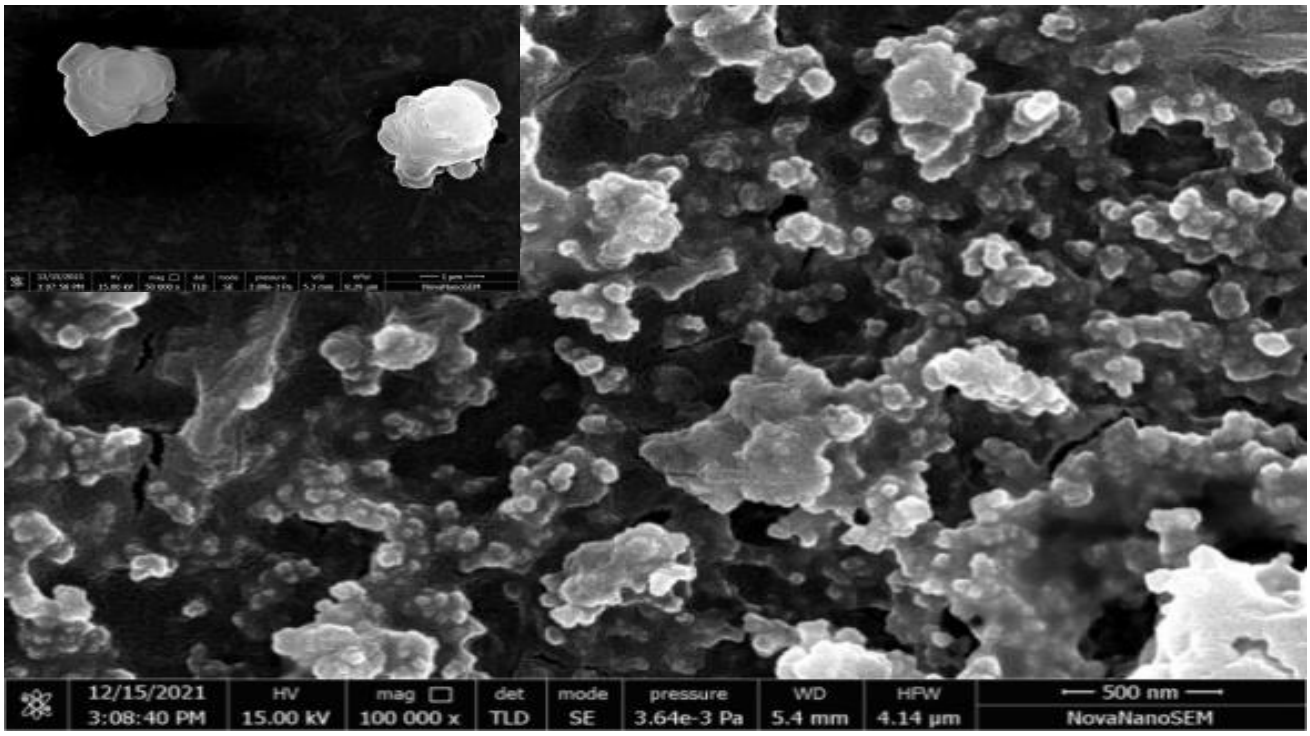
(d)



(e)

Fig.S15: Atomic Force Microscopic (AFM) Study of: (a) AgNPs at pH 11. (b) AgNPs at pH 7.40. (c) AgNPs after addition of Cysteine. (d) AgNPs after addition of Homocysteine. (e) AgNPs after addition of Glutathione.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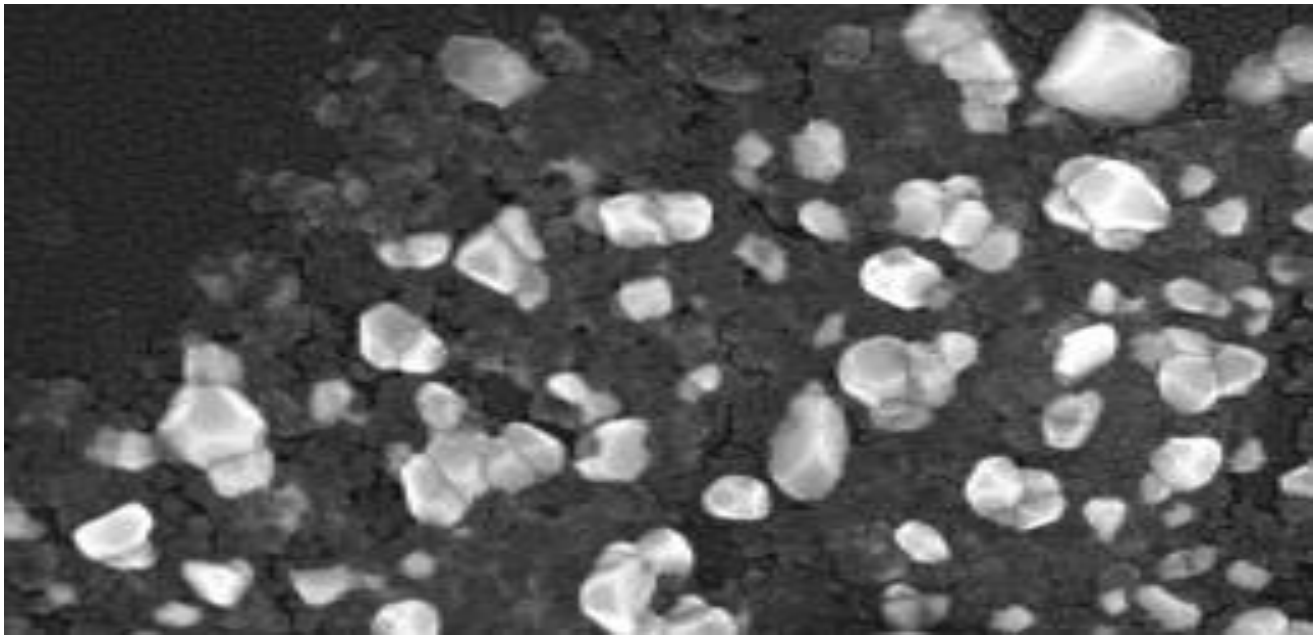
500 nm
NovaNanoSEM

(a)



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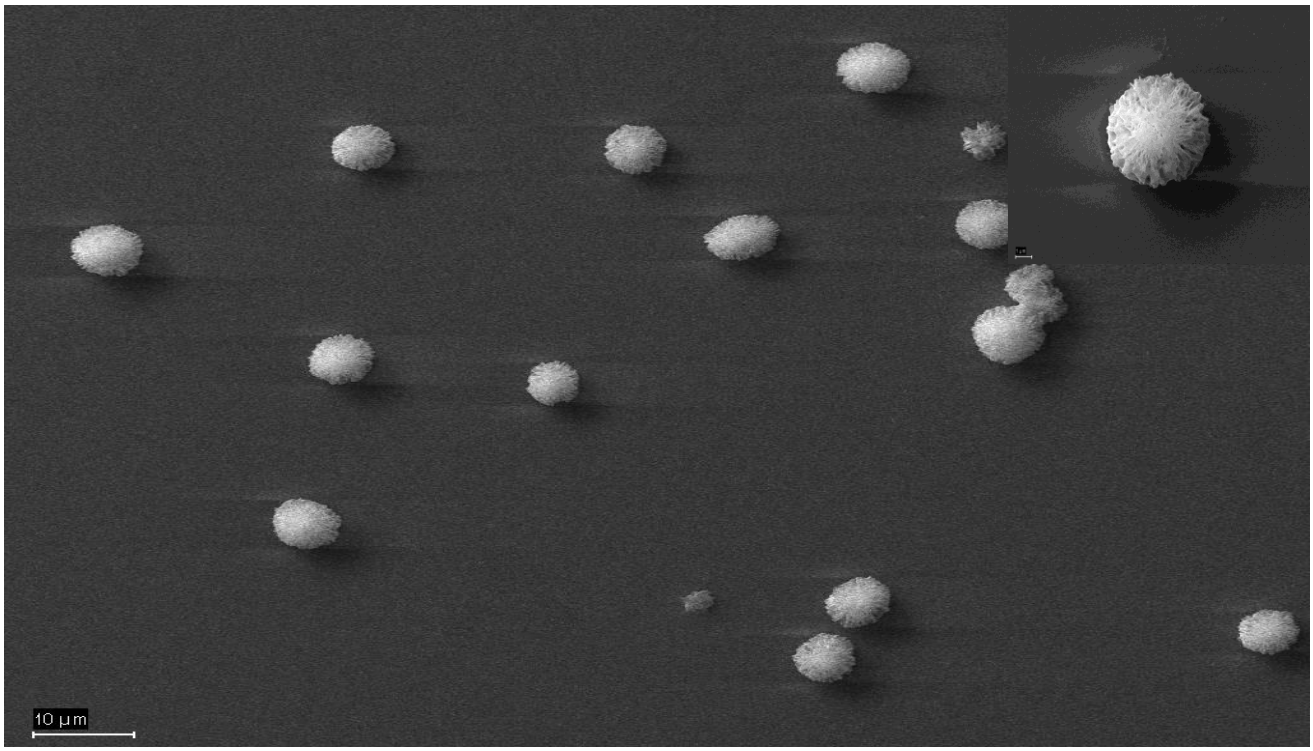

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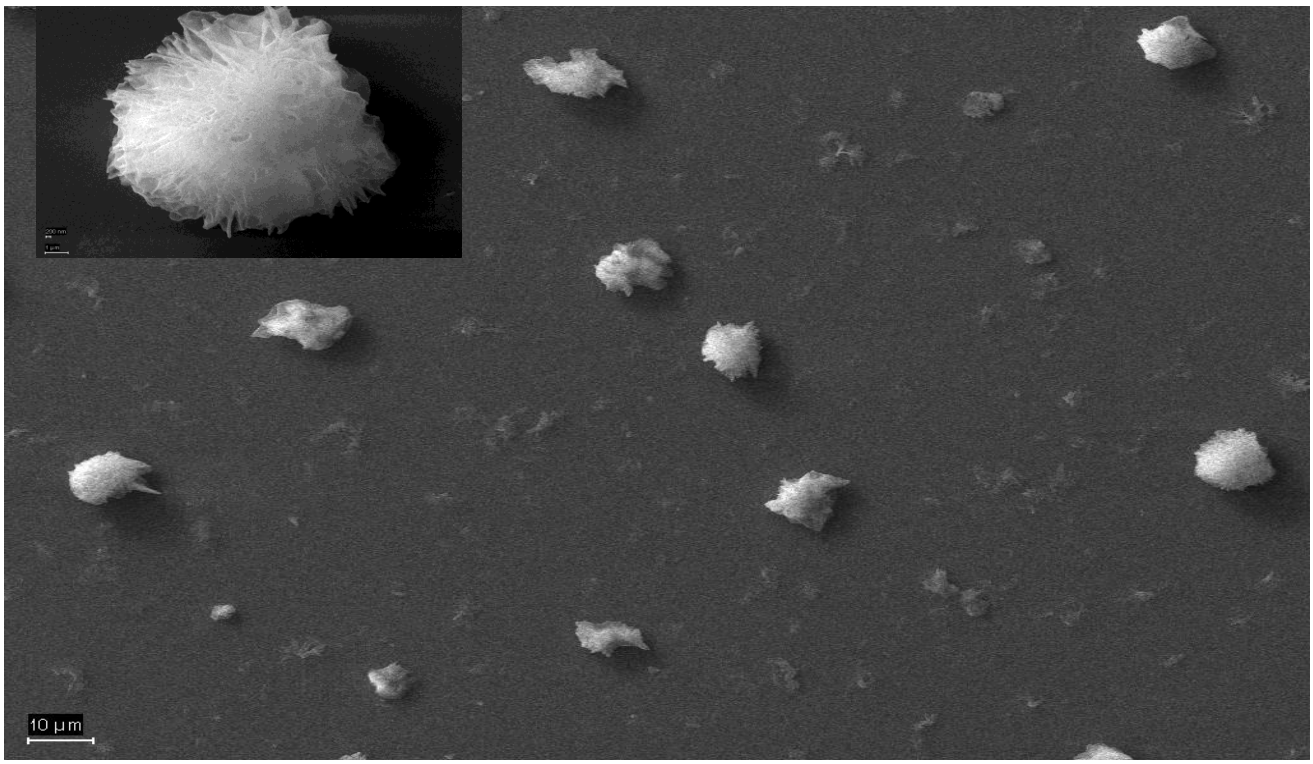

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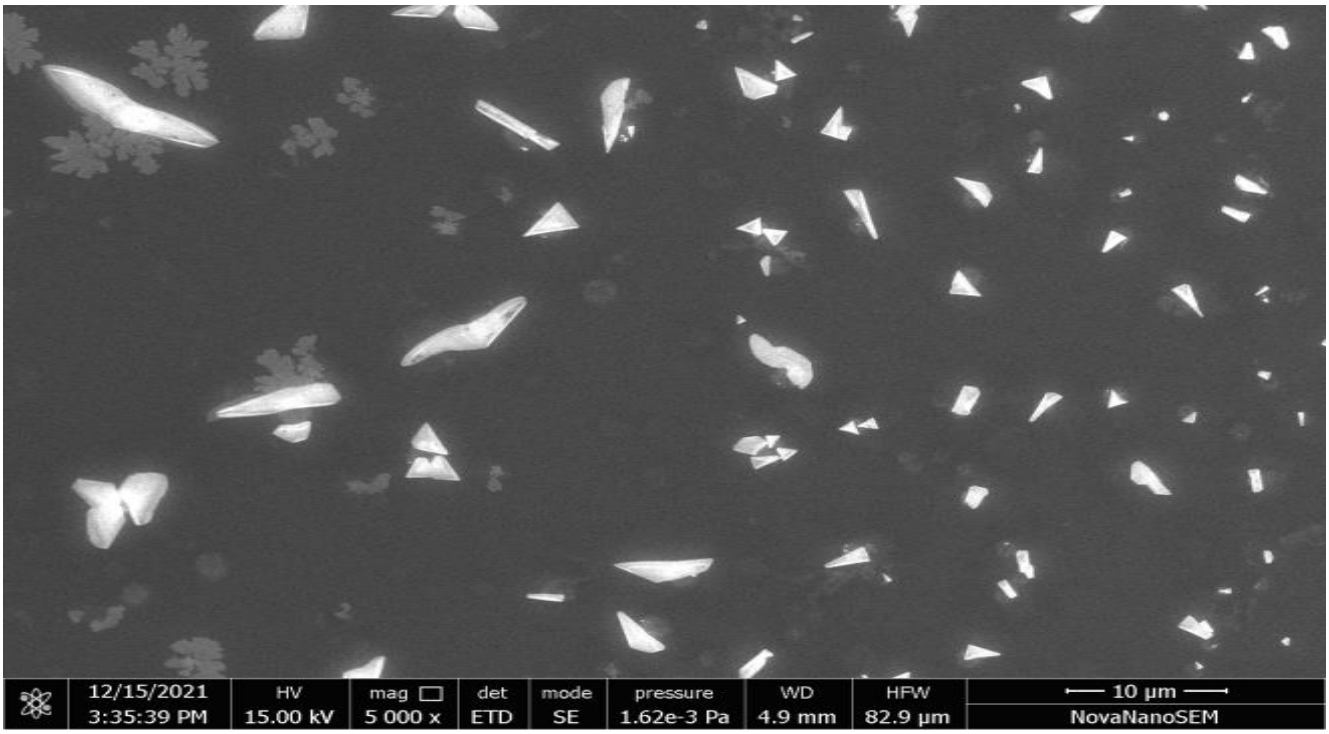
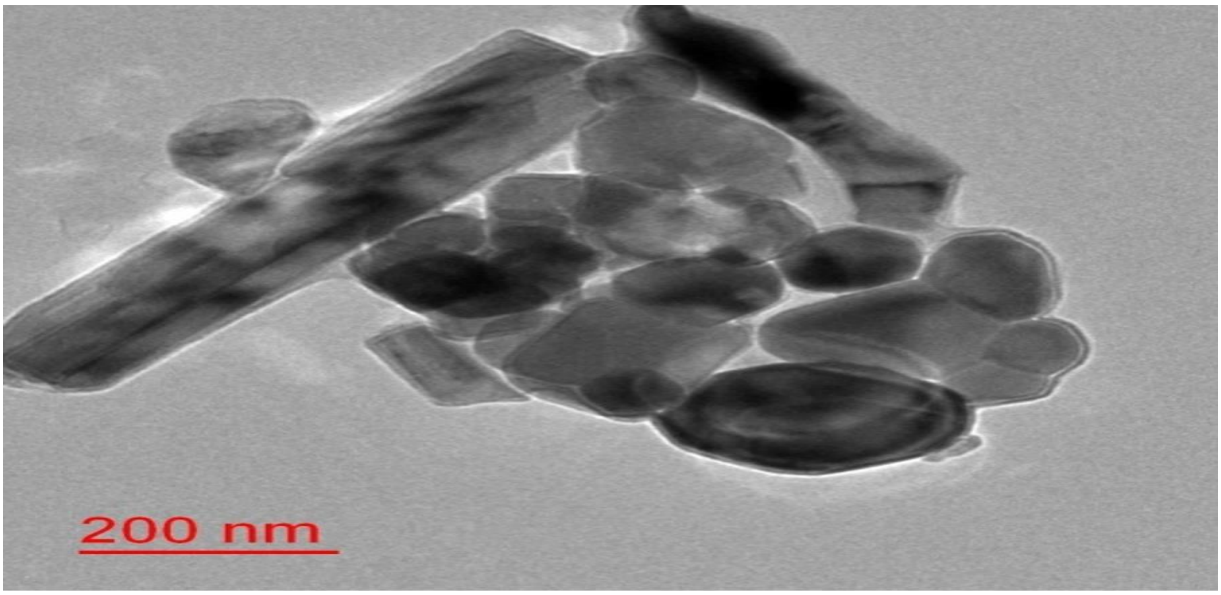
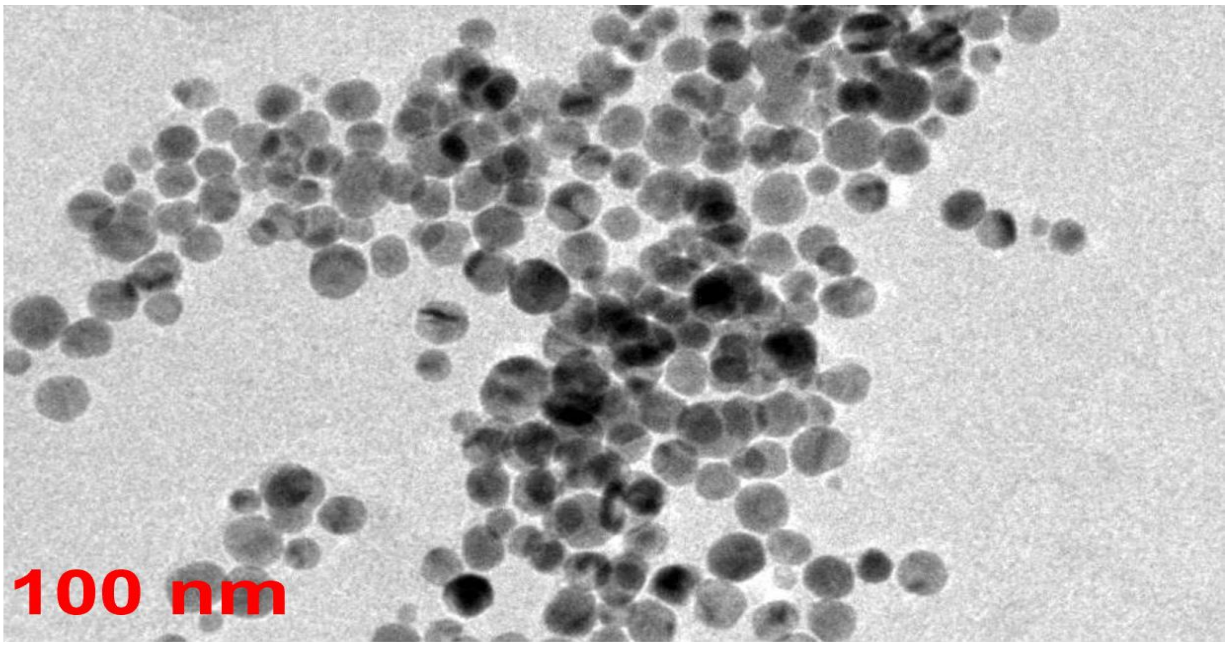


(e)

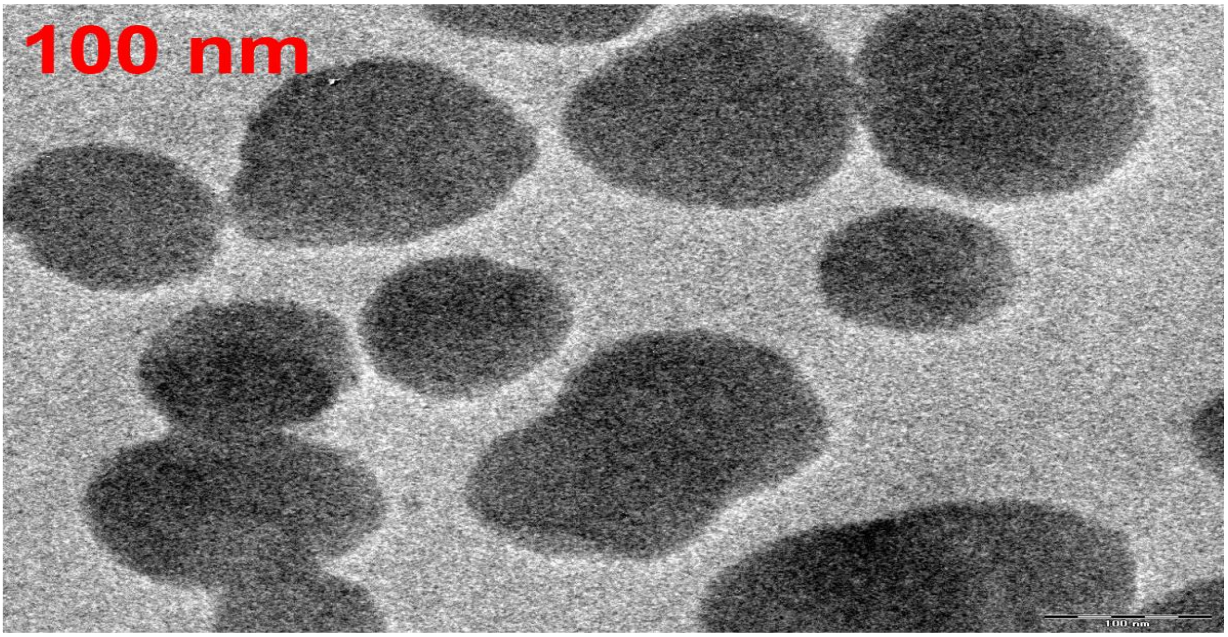
Fig.S16: FESEM images of: (a) AgNPs at pH 11. (b) AgNPs at pH 7.40. (c) AgNPs after addition of Cysteine. (d) AgNPs after addition of Homocysteine. (e) AgNPs after addition of Glutathione.



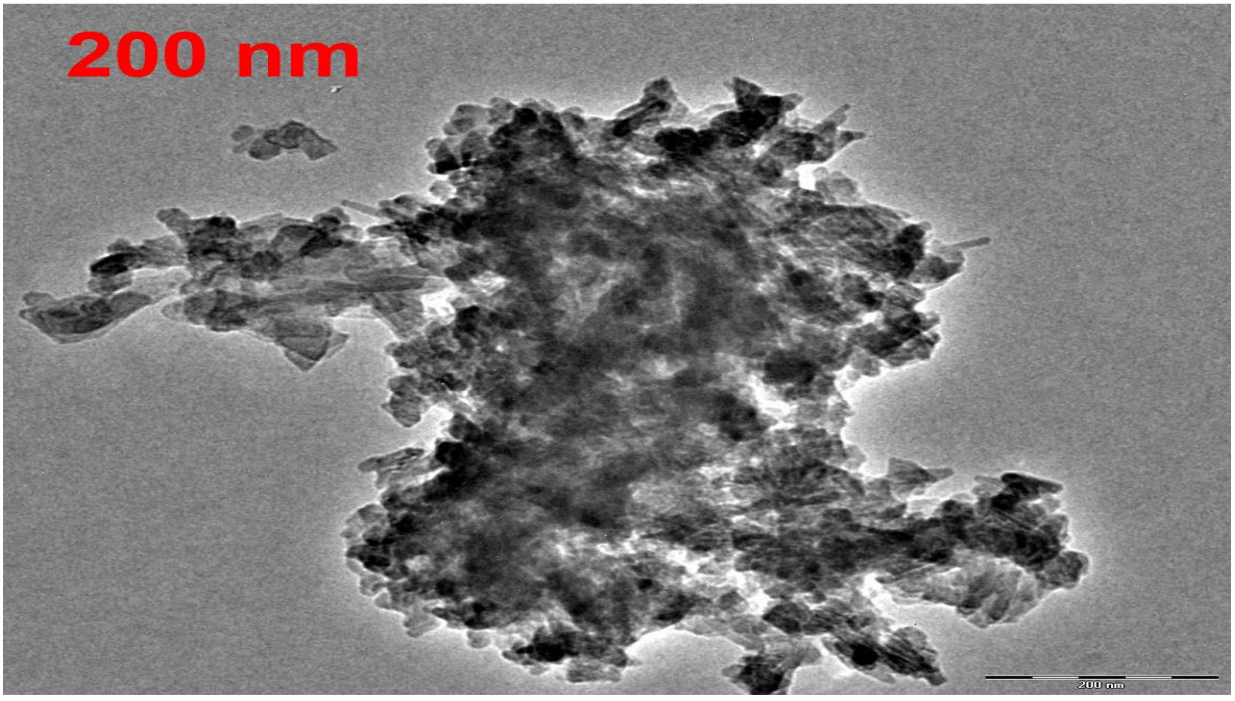
(a)



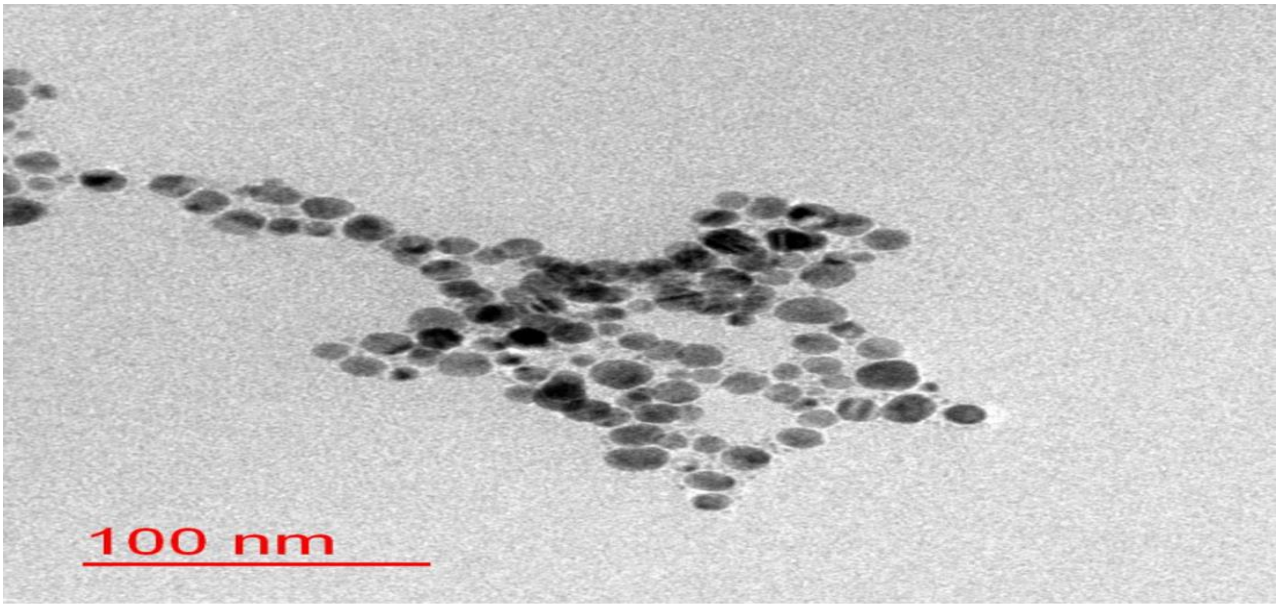
(b)



(c)

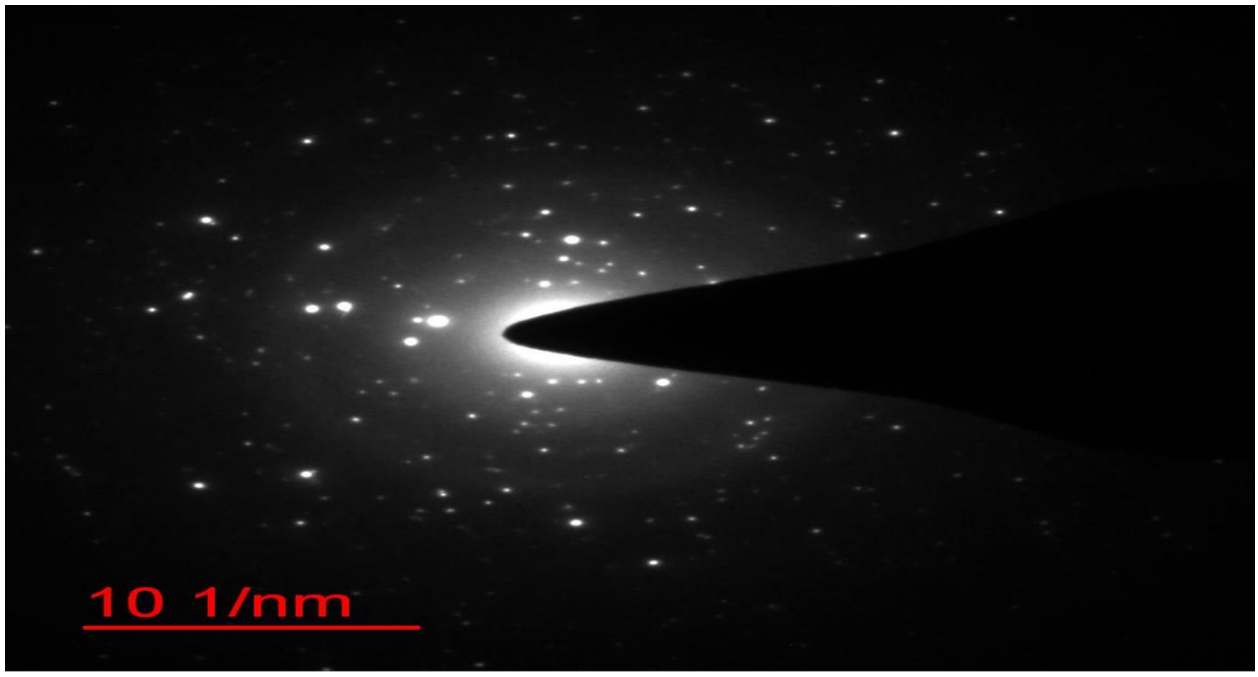


(d)

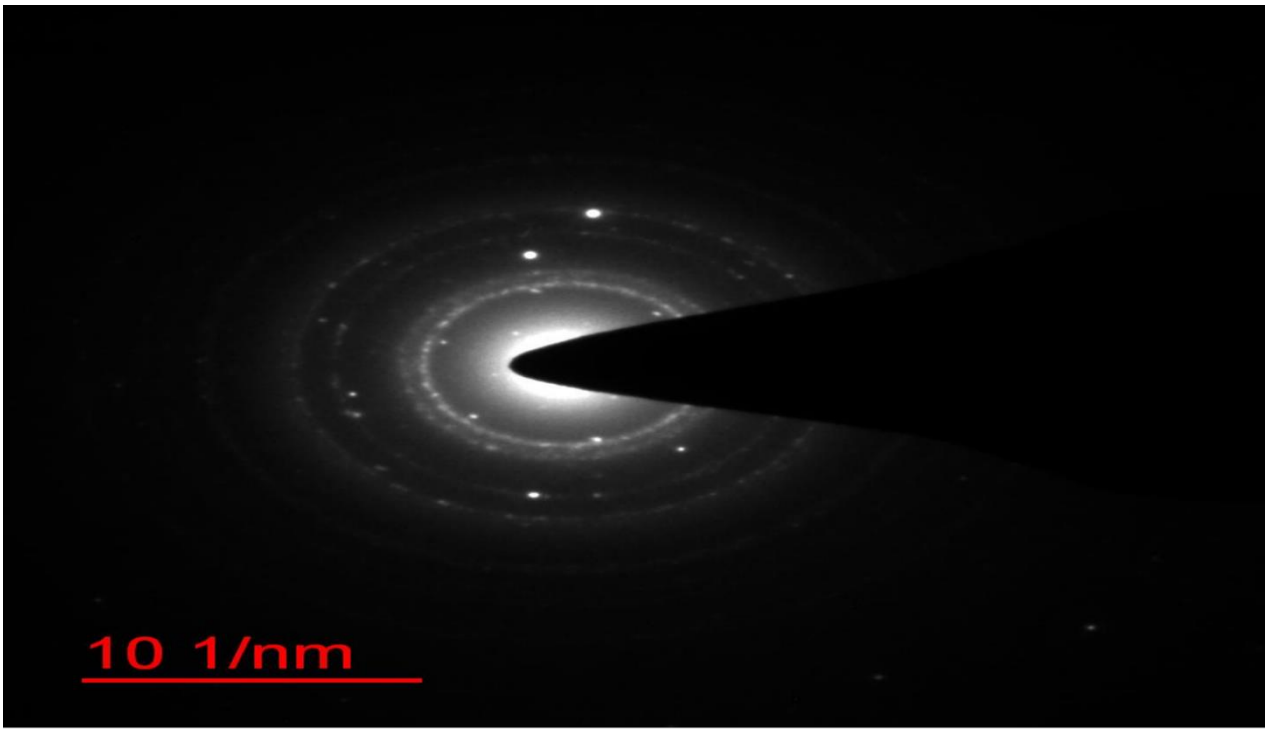


(e)

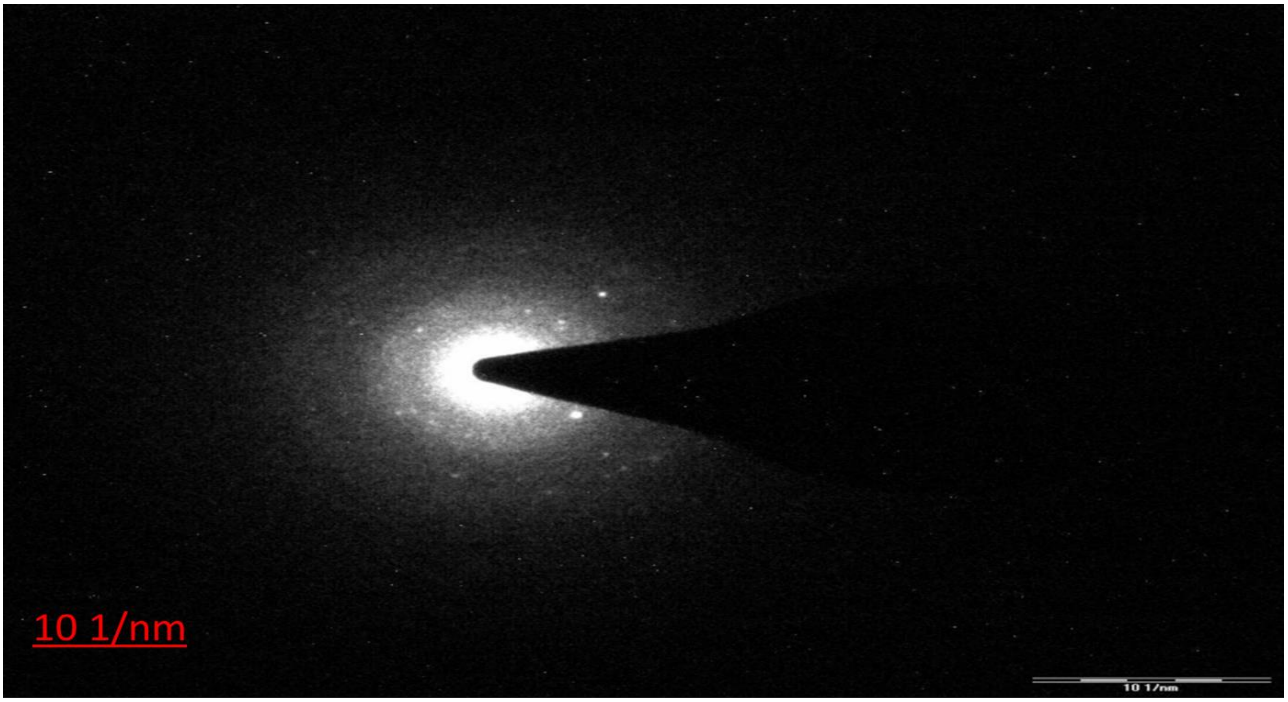
Fig.S17: HRTEM images of: (a) AgNPs at pH 11. (b) AgNPs at pH 7.40.(c) AgNPs after addition of Cysteine. (d) AgNPs after addition Homocysteine. (e) AgNPs after addition of Glutathione.



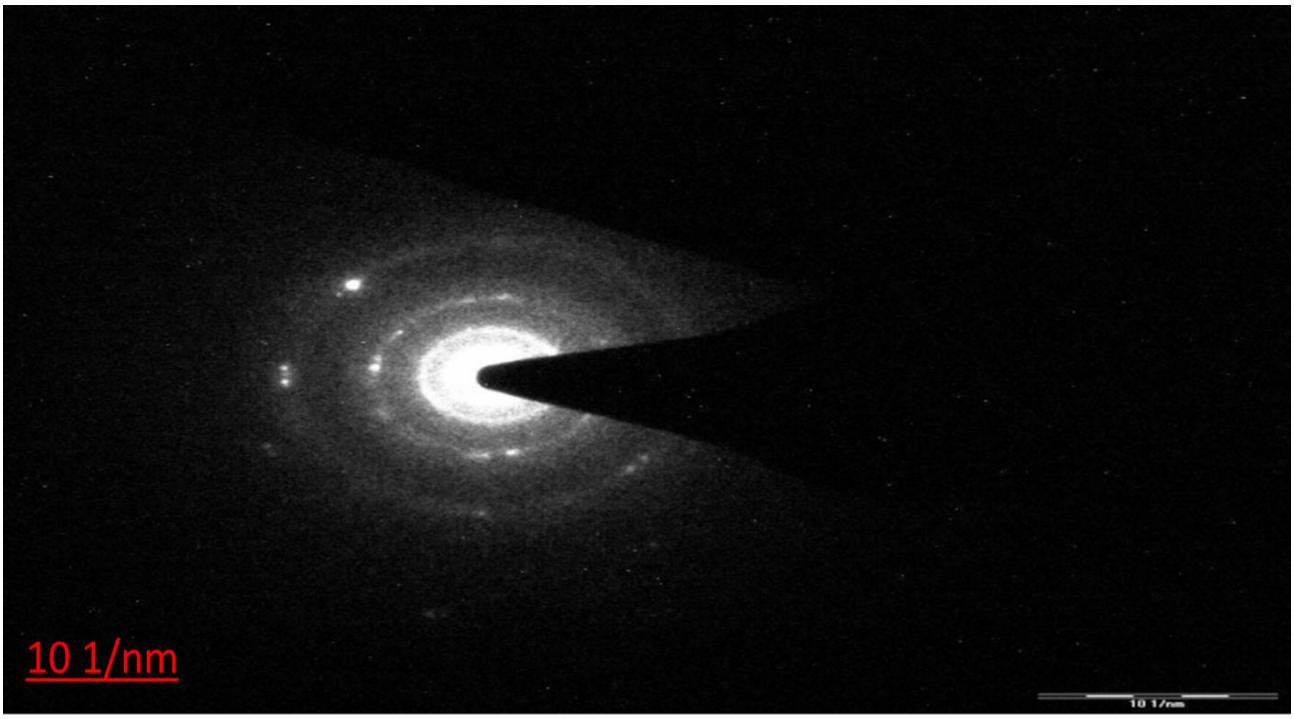
(a)



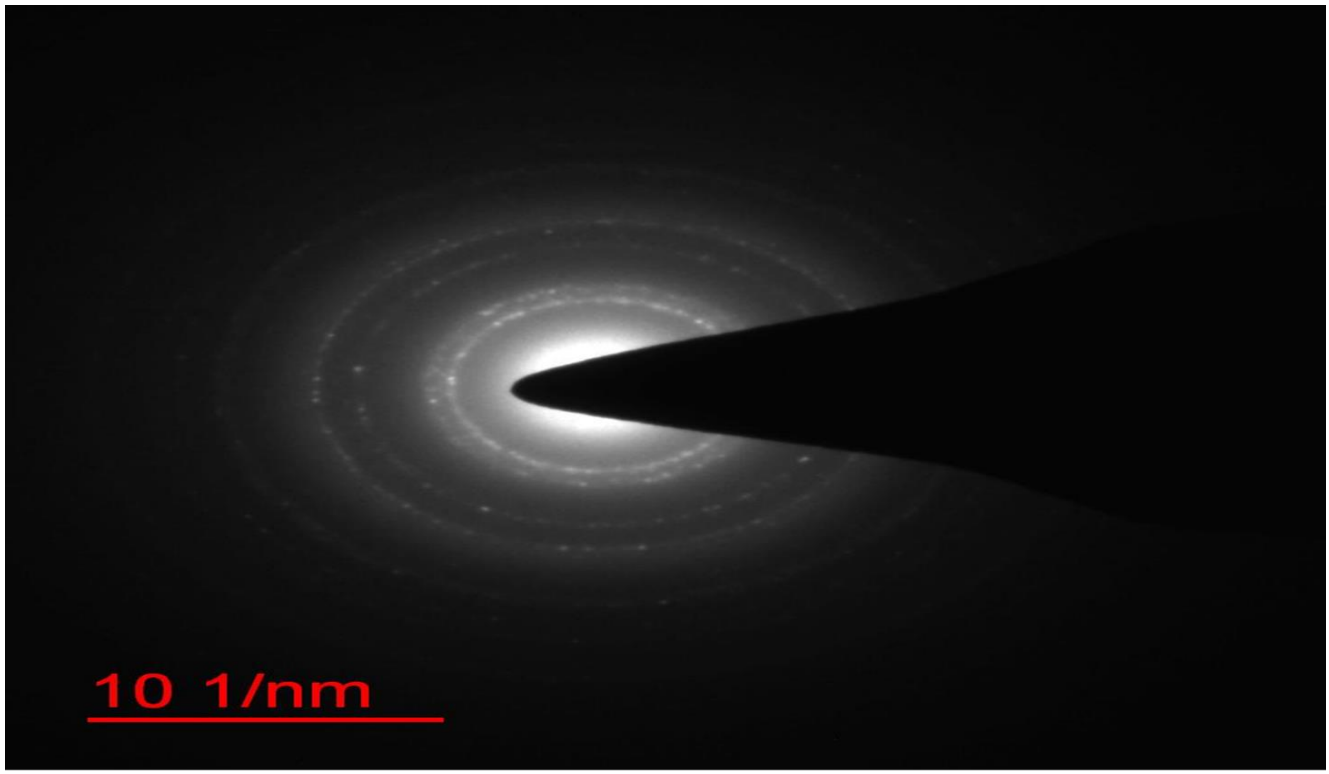
(b)



(c)

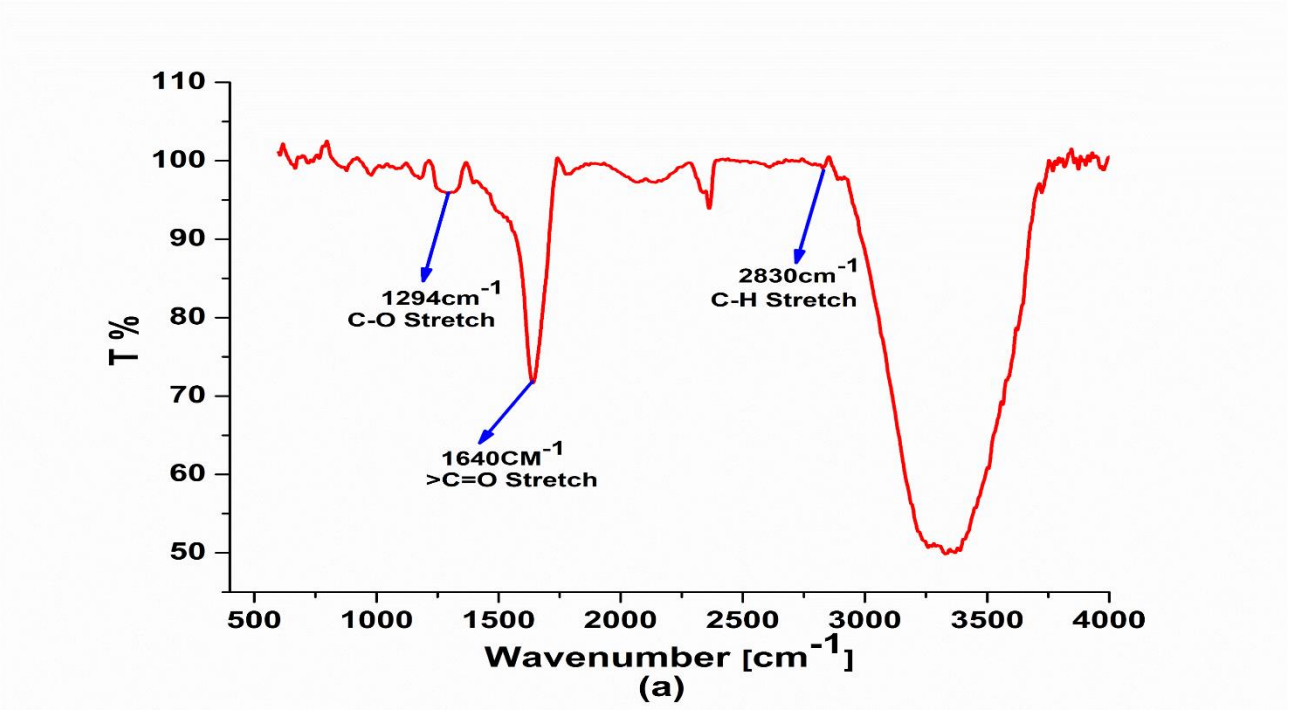


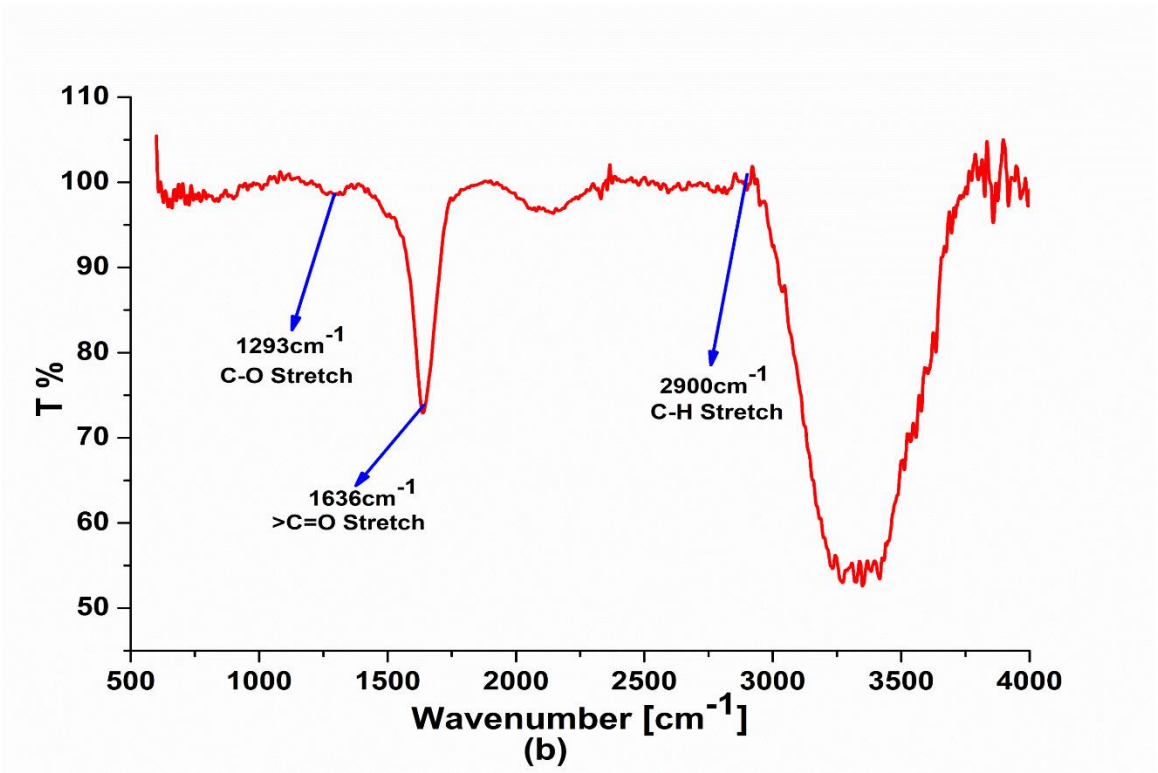
(d)

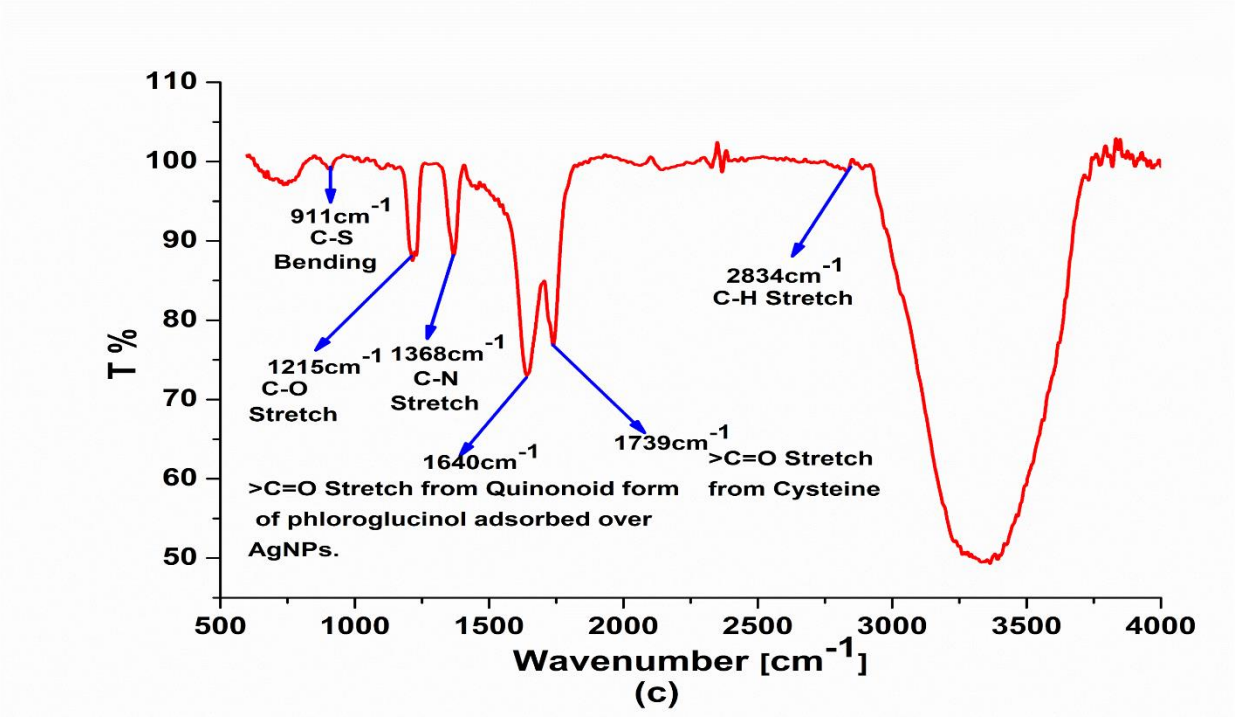


(e)

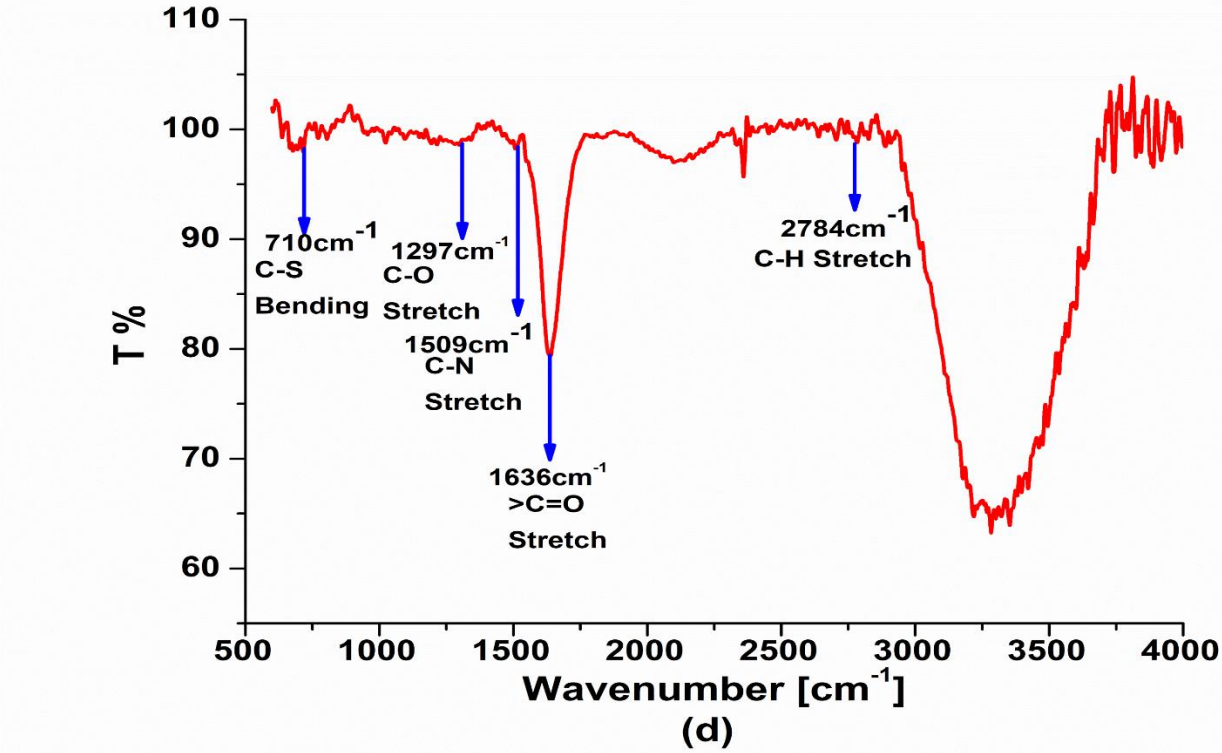
Fig.S18: SAED images of**:** (a) AgNPs at pH 11. (b) AgNPs at pH 7.40. (c) AgNPs after addition of Cysteine. (d) AgNPs after addition of Homocysteine. (e) AgNPs after addition of Glutathione.


110
100
90
80
70
60
50
T %
1294cm-1
C-O Stretch
1640CM-1
>C=O Stretch
2830cm-1
C-H Stretch
500
1000
1500
2000
2500
3000
3500
4000
Wavenumber [cm-1]
(a)


110
100
90
80
70
60
50
T %
1293cm-1
C-O Stretch
1636cm-1
>C=O Stretch
2900cm-1
C-H Stretch
500
1000
1500
2000
2500
3000
3500
4000
Wavenumber [cm-1]
(b)


T %
Wavenumber [cm-1]
911cm-1 C-S Bending
1215cm-1 C-O Stretch
1368cm-1 C-N Stretch
1640cm-1 >C=O Stretch from Quinonoid form of phloroglucinol adsorbed over AgNPs.
1739cm-1 >C=O Stretch from Cysteine
2834cm-1 C-H Stretch

(c)


T %
Wavenumber [cm-1]
710cm-1 C-S Bending
1297cm-1 C-O Stretch
1509cm-1 C-N Stretch
1636cm-1 >C=O Stretch
2784cm-1 C-H Stretch

(d)

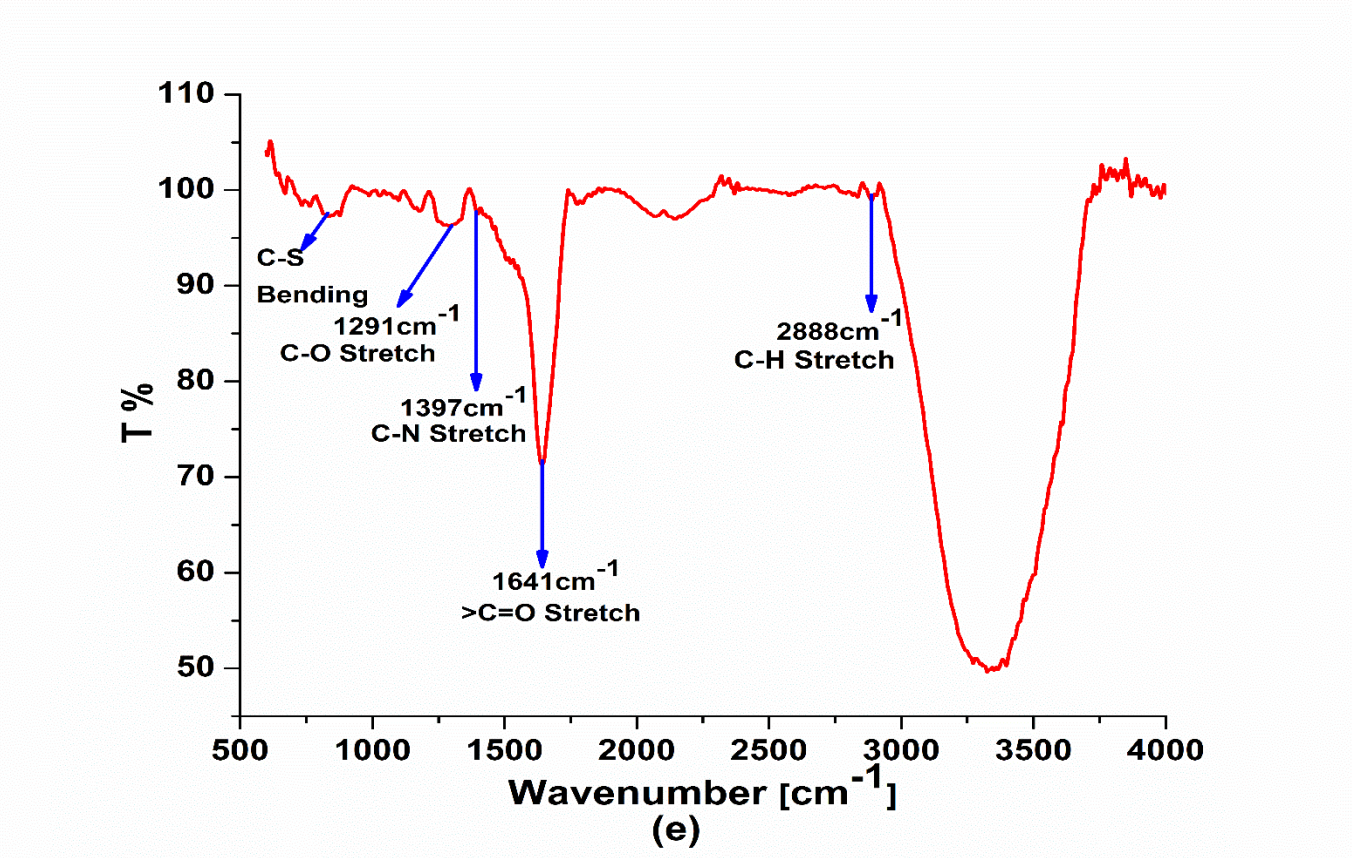


Fig.S19: IR Spectral Patterns for: (a) AgNPs at pH 11. (b) AgNPs at pH 7.40.(c) AgNPs after addition of Cysteine. (d) AgNPs after addition of Homocysteine. (e) AgNPs after addition of Glutathione.

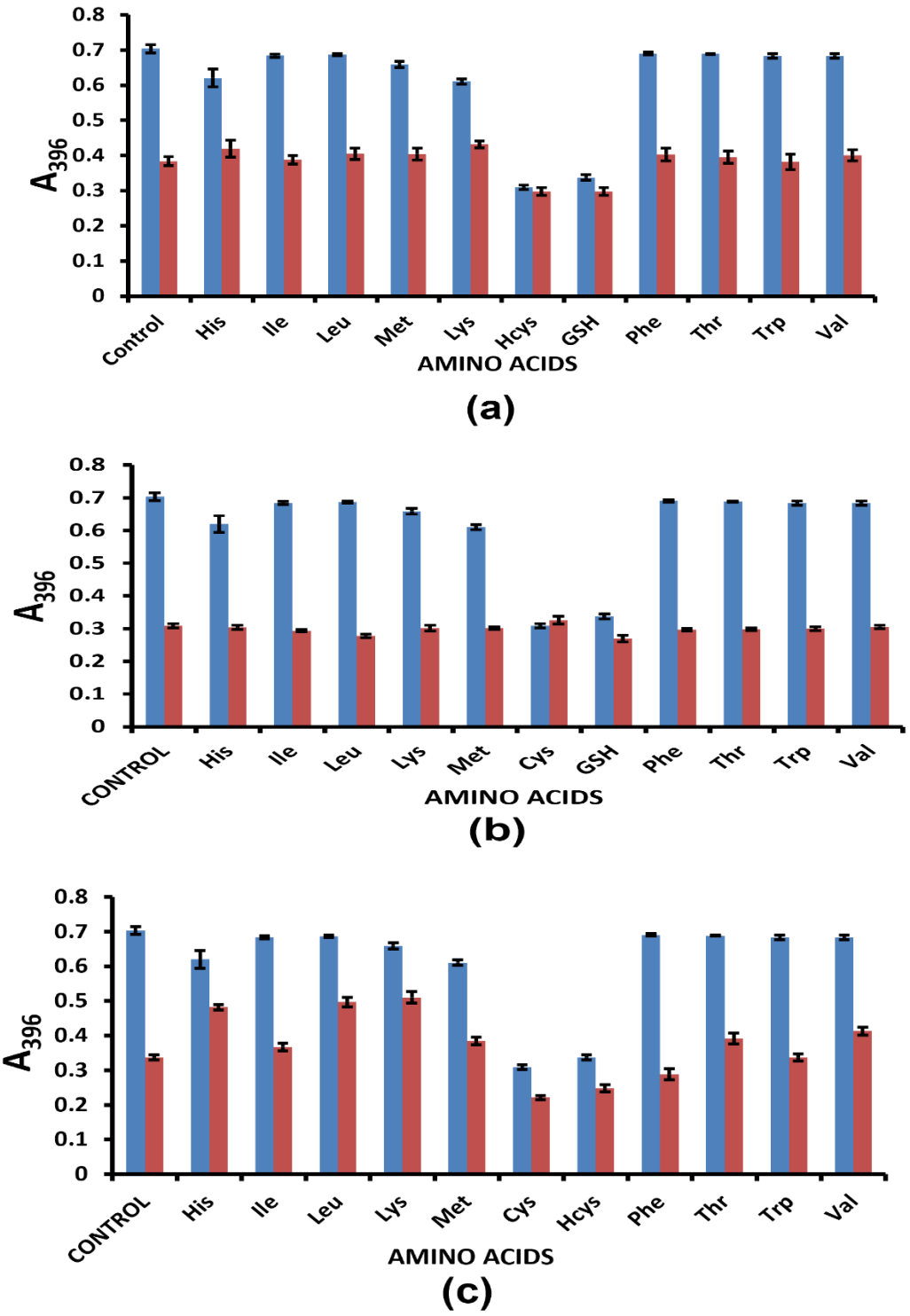


Fig.S20: Interference studies for AgNPs (at 396 nm, pH 7.4) with different essential amino acids. (a) Blue bar: AgNPs + amino acids,red bar: AgNPs + amino acids +Cysteine.(b) Blue bar: AgNPs + amino acids, red bar: AgNPs + amino acids + Homocysteine.(c) Blue bar: AgNPs + amino acids, red bar: AgNPs+amino acids + Glutathione

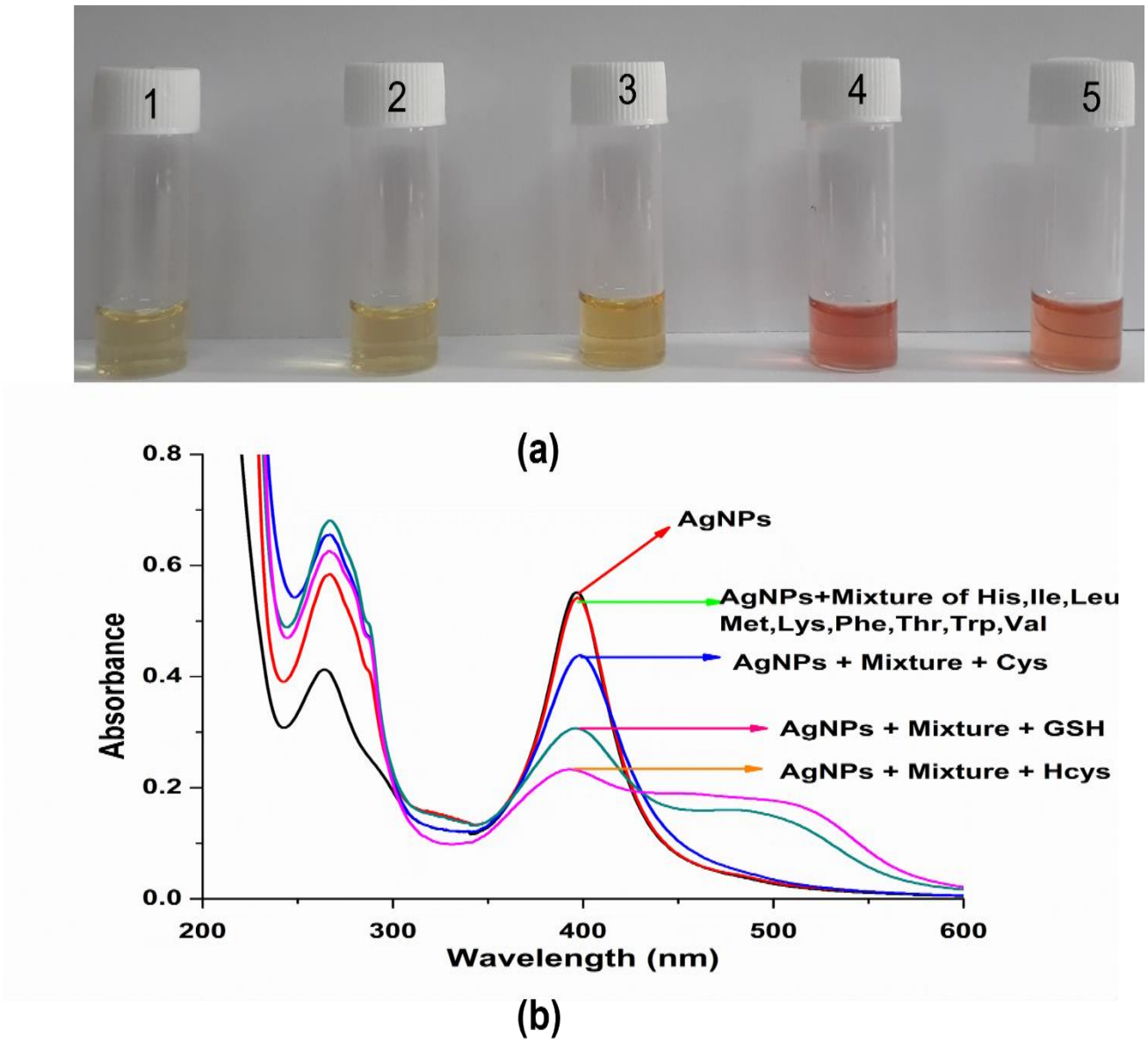


Fig.S21: Matrix study: (a): Visual responses (1) AgNPs (2) AgNPs + Mixture (solution) containing different amino acids i.e. His,Ile,Leu,Met,Lys,Phe,Thr,Trp,Val. (3) AgNPs + Mixture + Cysteine. (4) AgNPs + Mixture + Homocysteine. (5) AgNPs + Mixture + Glutathione. (b) UV-Visible spectra of corresponding visual responses.

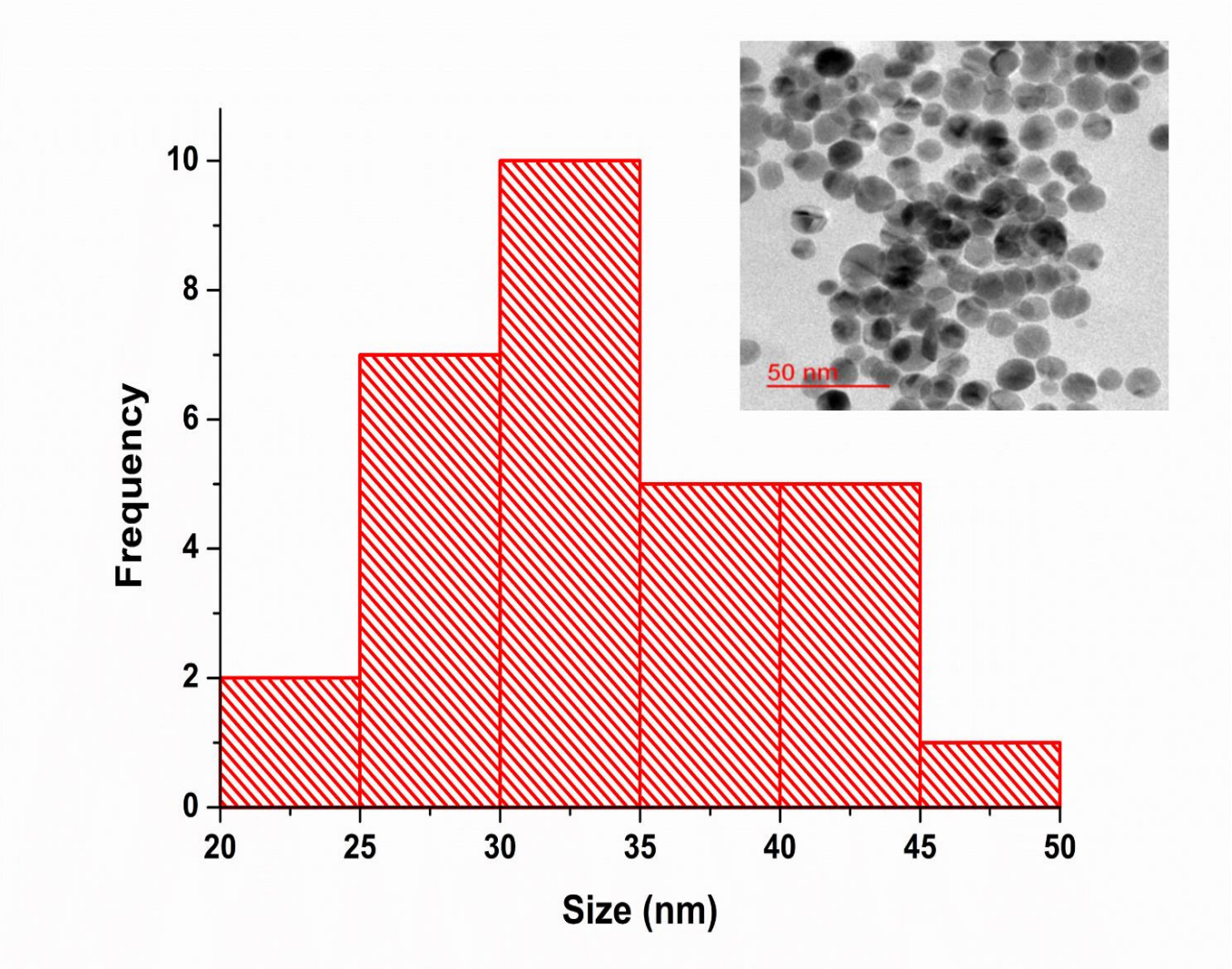


Fig.S22: Histogram image showing size distribution of AgNPs (at pH 7.4); TEM image attached

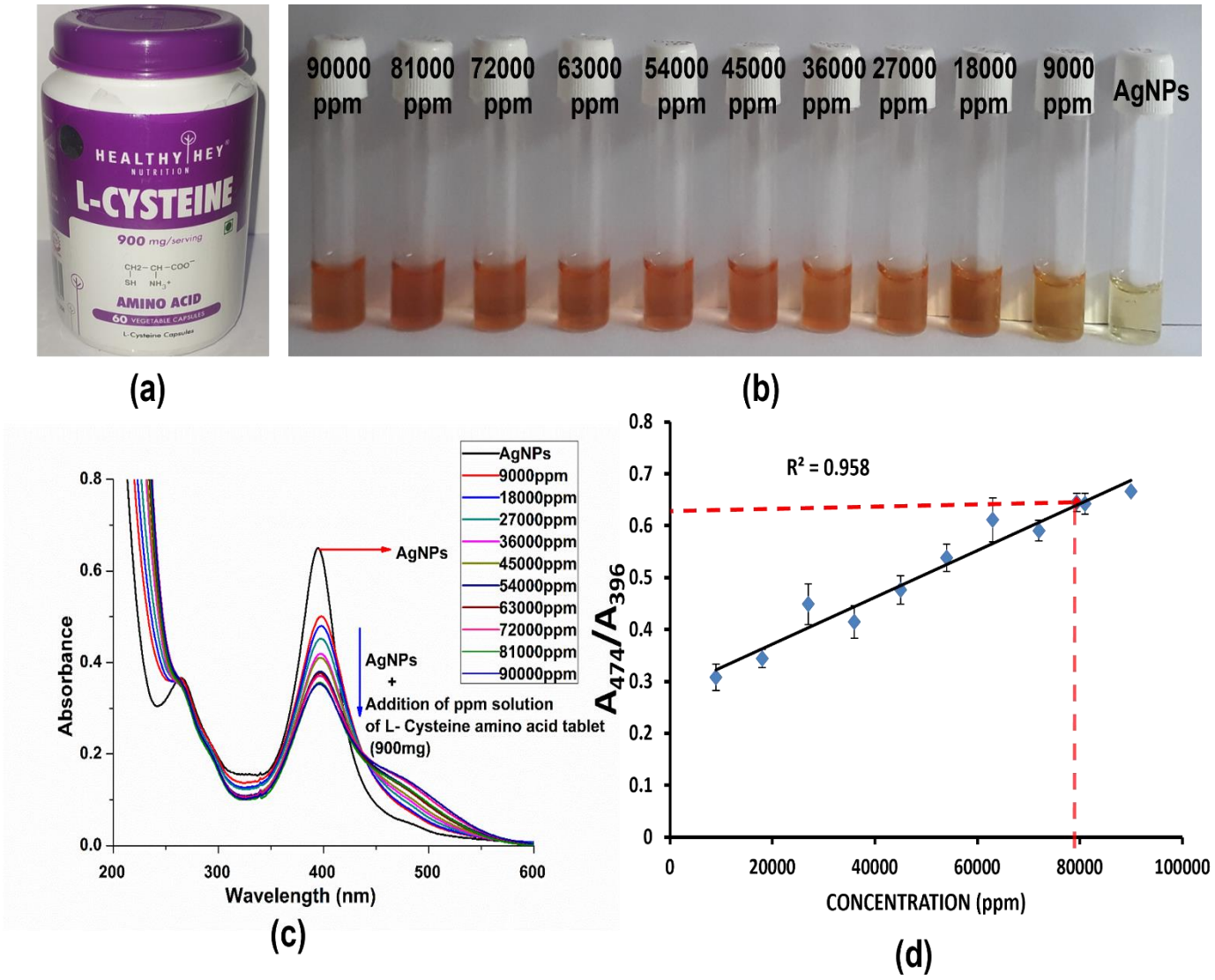


Fig.S23: Study of real sample containing Cysteine **(HEALTHY HEY Nutrition)**: (a) Image of **(HEALTHY HEY Nutrition)** L-Cysteine(900mg) containing capsules. (b) visual response of AgNPs with L-Cysteine capsule at different ppm (from 9000ppm-90000ppm) solutions. (c) UV-Visible spectra of different ppm solutions after addition to AgNPs. (d) Calibration plot [ratio of absorbance (A_{474}/A_{396}) as ordinate while concentration of L-cysteine (ppm) on abscissa] for the quantification of Cysteine in **(HEALTHY HEY Nutrition).**

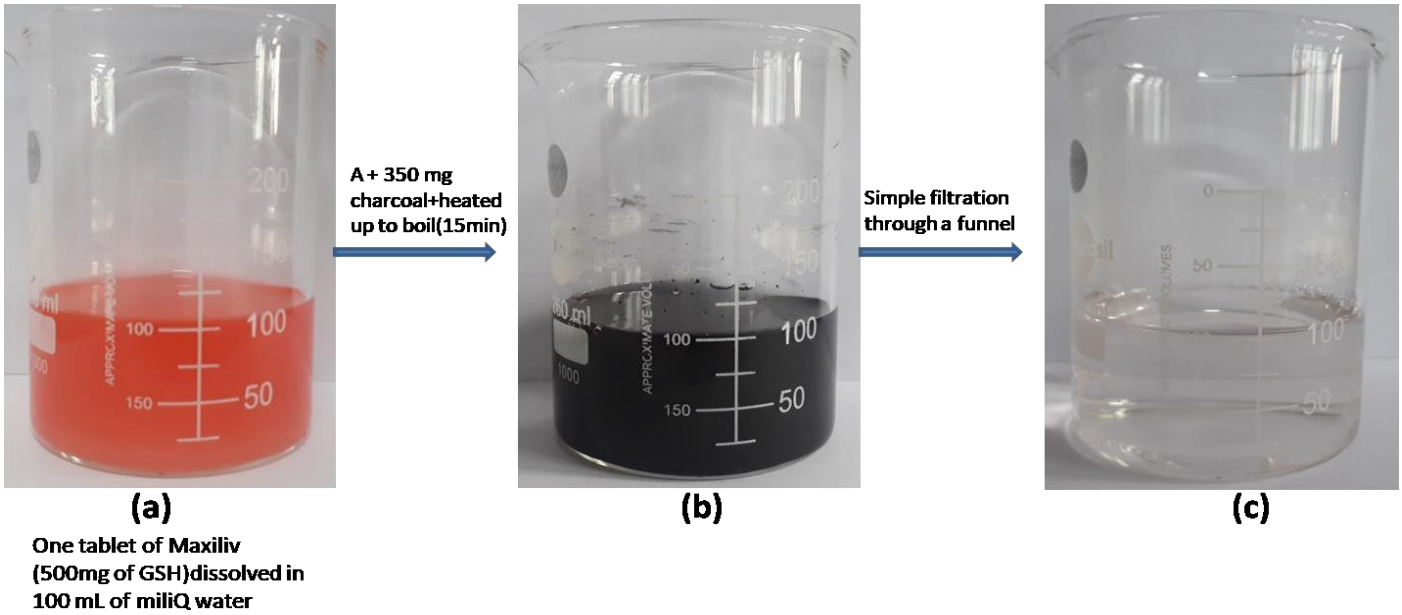


Fig.S24: Diagram showing sample preparation of Maxiliv Tablet for the visual and quantification of Glutathione.

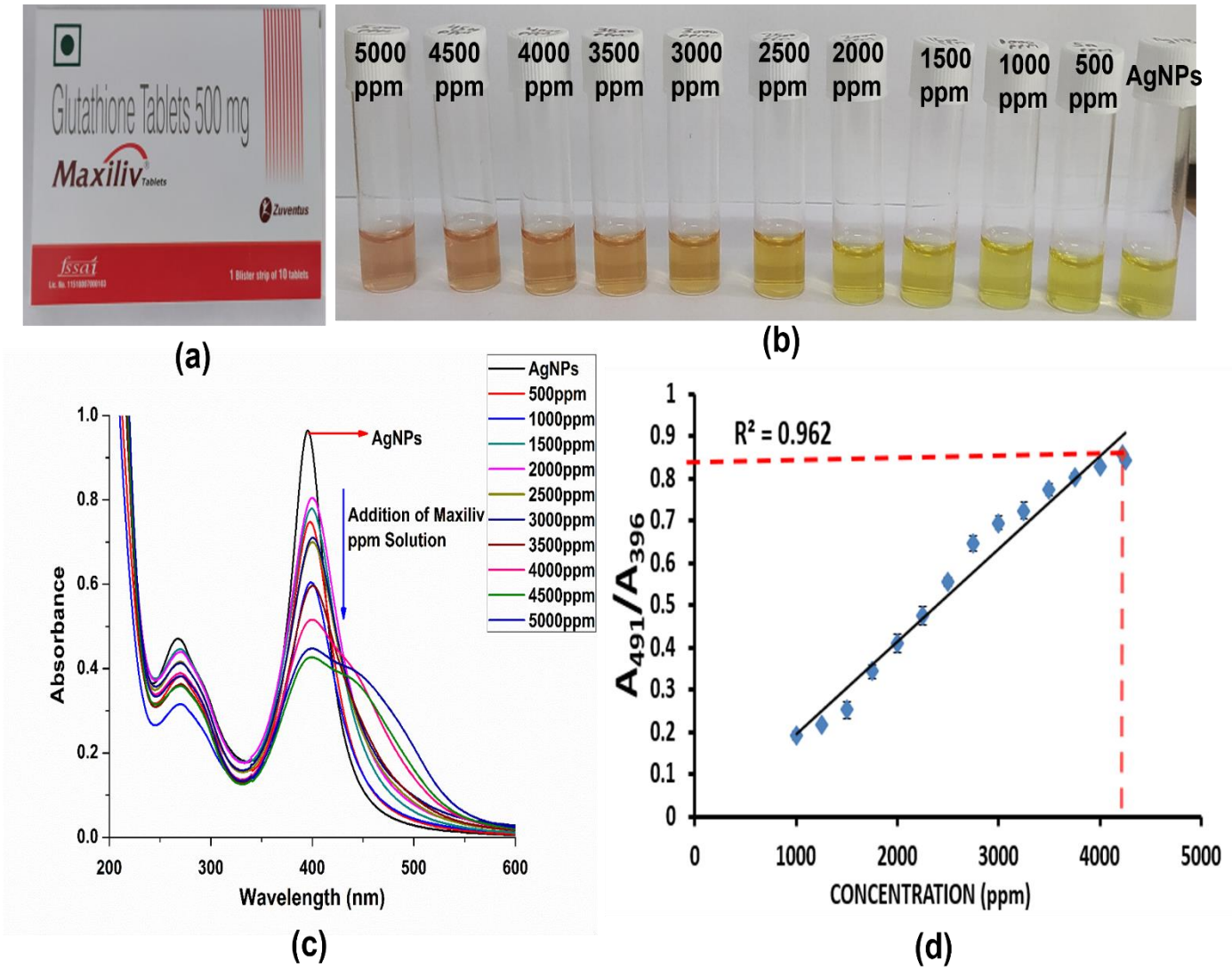


Fig.S25: Study of yet another real sample containing Glutathione (Maxiliv) (a) Image of Maxiliv tablet (500mg) of Glutathione. (b) Visual response of AgNPs at different ppm solution of Maxilivtablet (from 500ppm to 5000 ppm). (c) UV-Visible spectra of different ppm solution after addition to AgNPs. (d) Calibration plot [(A_{491}/A_{396}) as the ordinate and concentration(ppm) as abscissa] for the quantification of Glutathione in (Maxiliv tablet).

Fig.S26(a): Probable mechanism for the synthesis of Phloroglucinol sensitized silver nanoresonators.

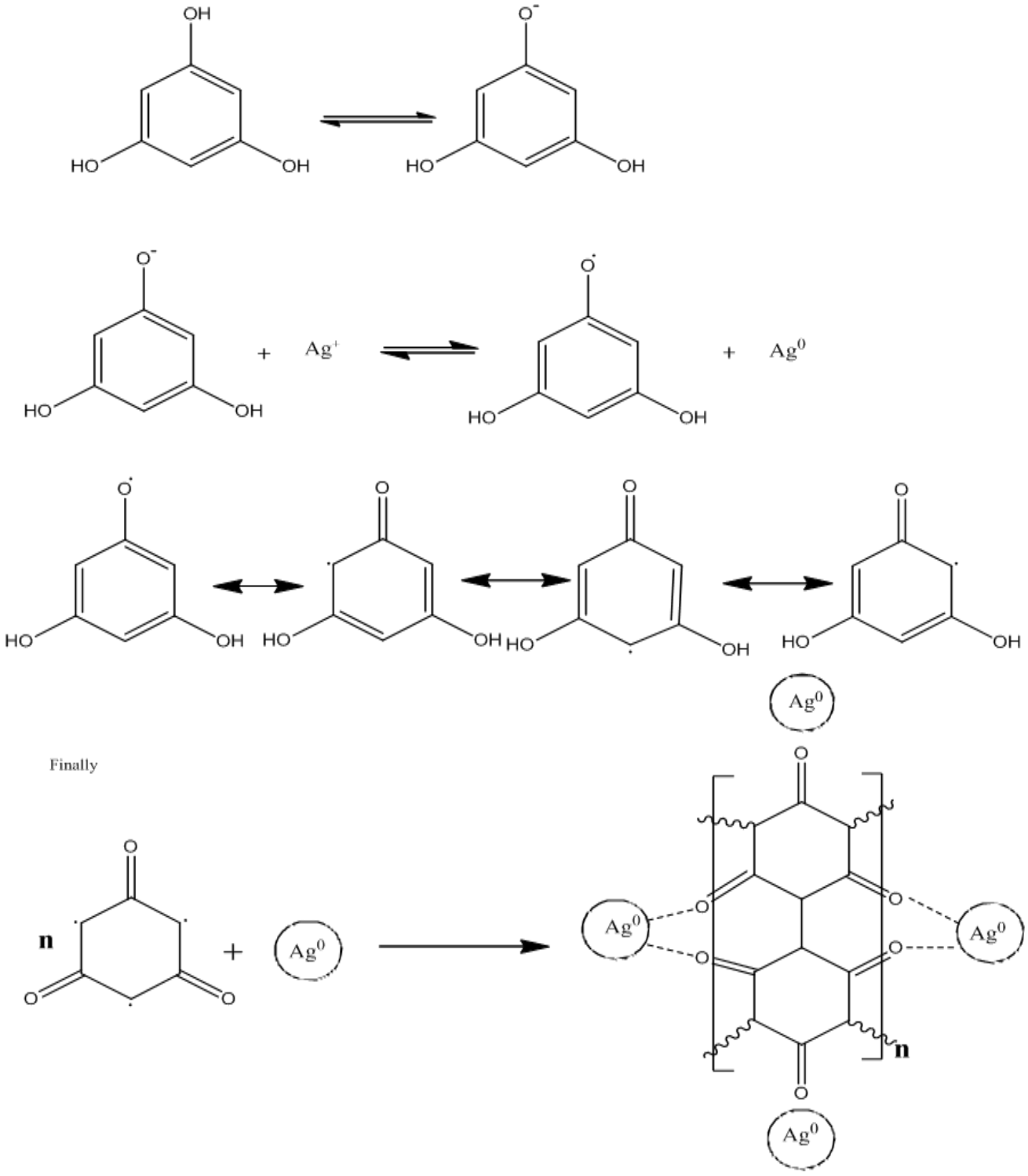
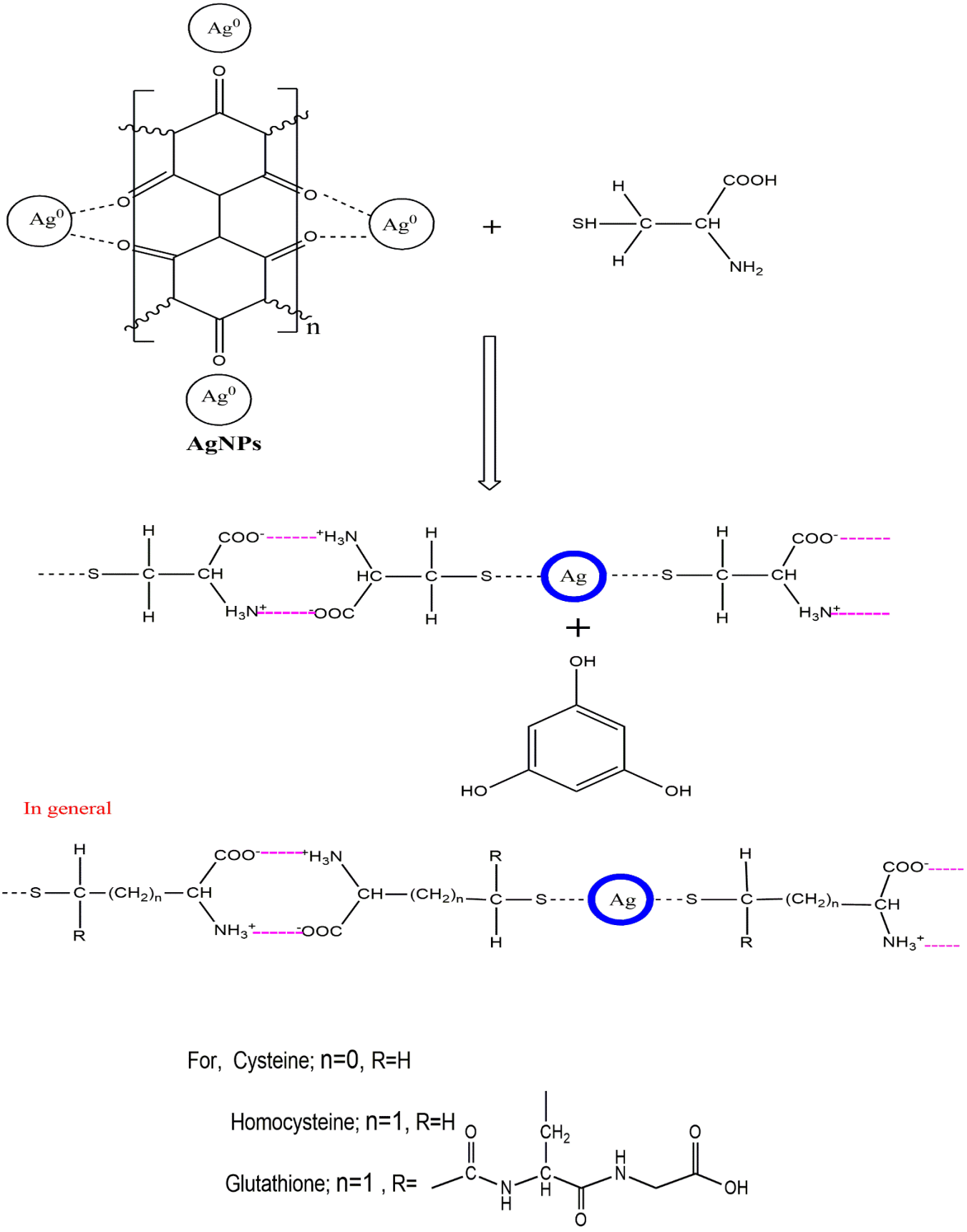
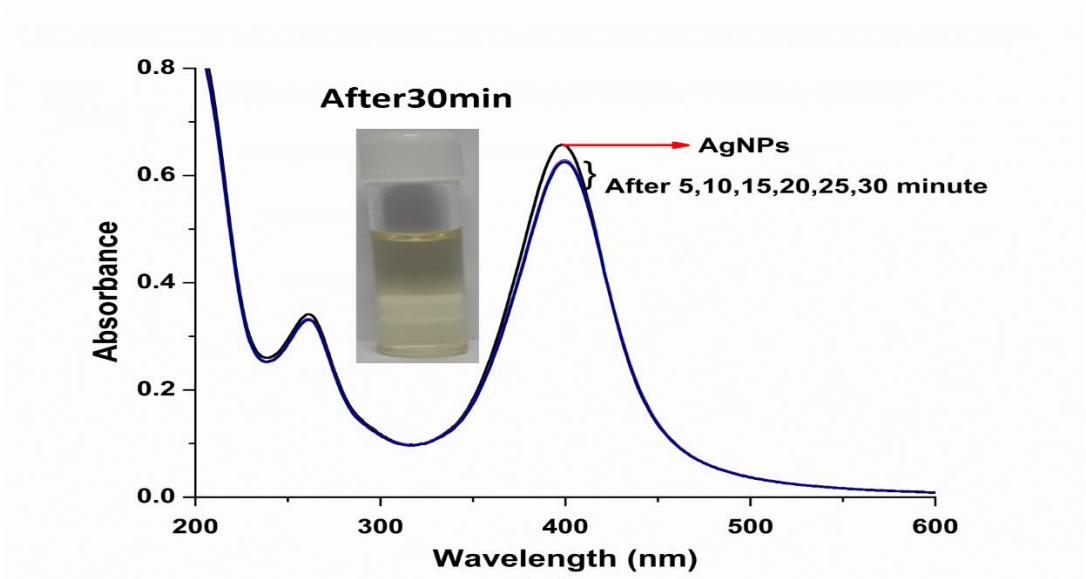
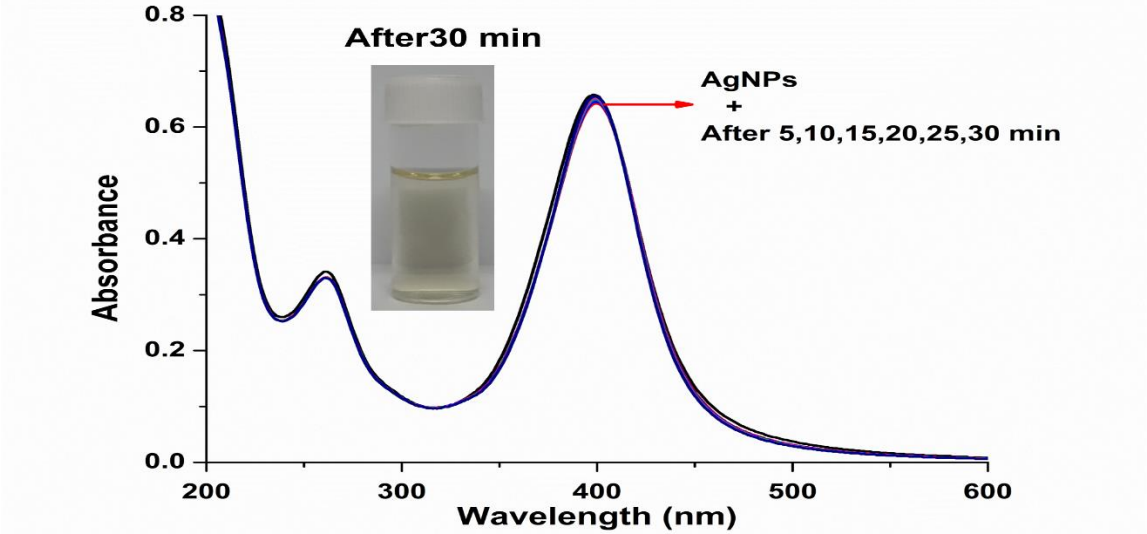


Fig.S26(b): Probable mechanism for the interaction of AgNPs with Cys, Hcys and GSH.

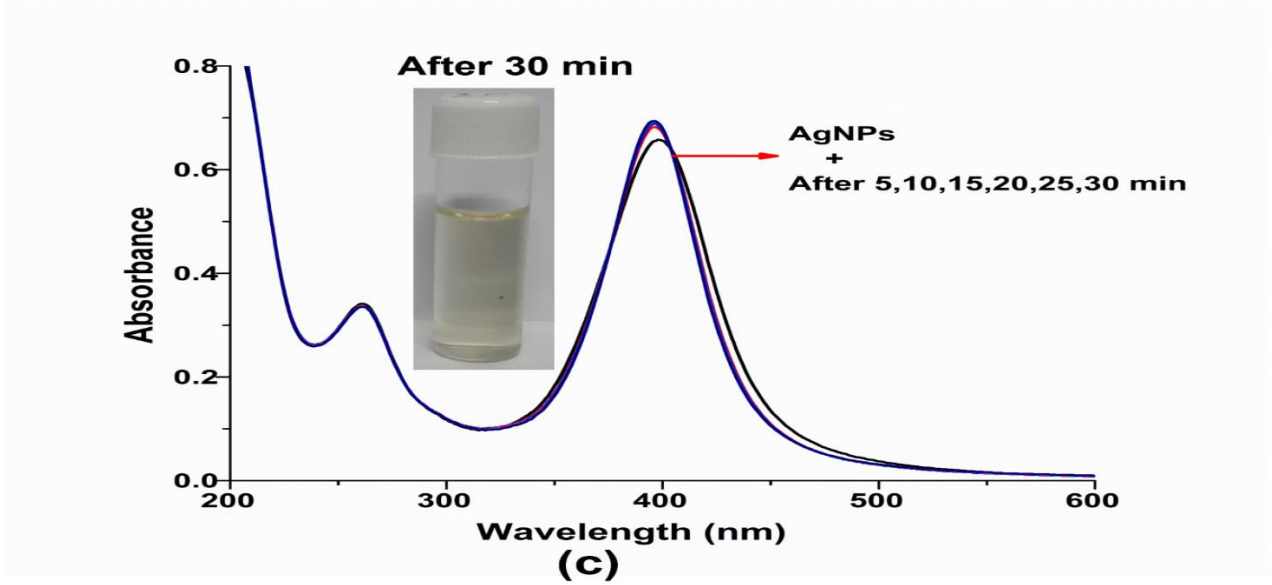



After30min
AgNPs
After 5,10,15,20,25,30 minute
Absorbance
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
200
300
400
500
600

(a)


After30 min
AgNPs
+
After 5,10,15,20,25,30 min
Absorbance
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
200
300
400
500
600

(b)



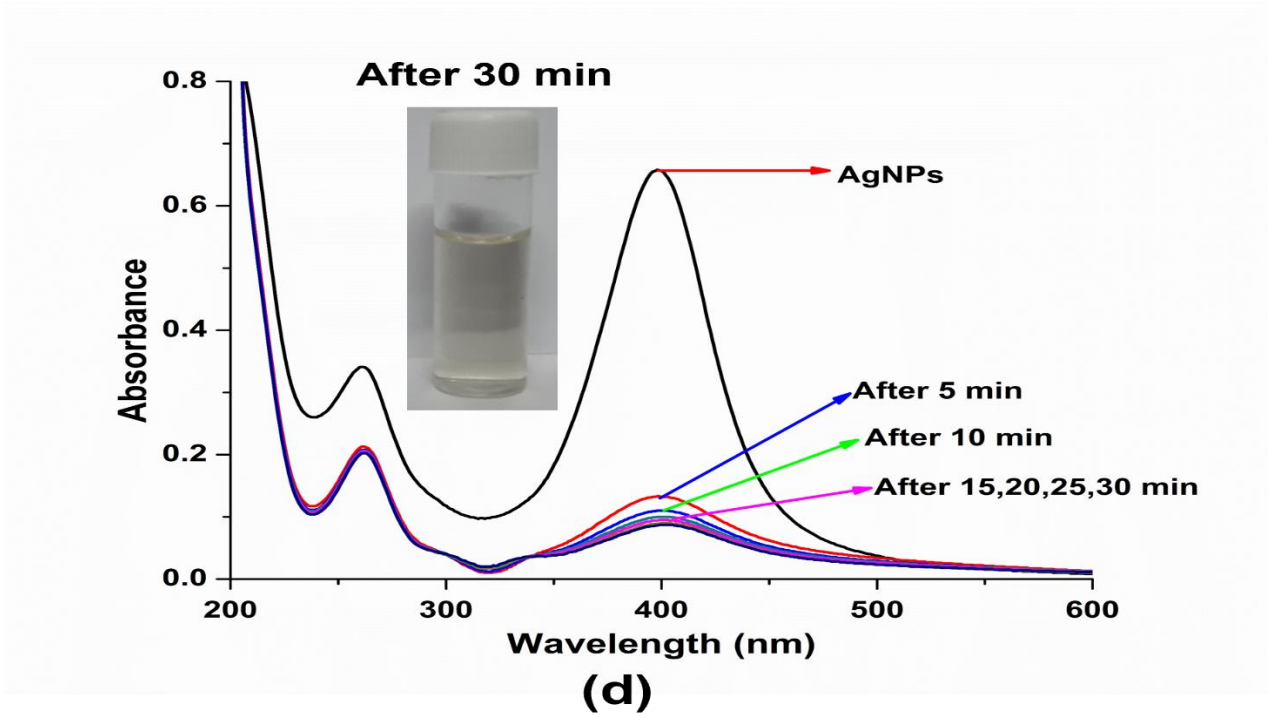


Fig.S27: Stability check through the electrolyte (NaCl) addition (a) 0.01M and corresponding UV-Visible spectra at the interval of 5 min. (b) 0.1M and corresponding UV-Visible spectra at the interval of 5 min. (c) 1M and corresponding UV-Visible spectra at the interval of 5 min. (d) 2M and corresponding UV-Visible spectra at the interval of 5 min.

Table S1: Showing comparison of LOD's in present case with similar previous studies.

	Analytes	LOD	References
1.	Cysteine Homocysteine	0.16 μM 0.25 μM	1
2.	Cysteine Homocysteine Glutathione^{-}	0.079 μM 0.041 μM 0.086 μM	2
3.	Cysteine Homocysteine	1.14×10^{-6} 0.64×10^{-7}	3
4.	Cysteine Homocysteine Glutathione	50 nM 10 nM 100 nM	4
5.	Cysteine Homocysteine Glutathione	260 nM 10 nM 4.11 nM	5
6.	Cysteine Homocysteine Glutathione	4.1μM 0.16μM 3.1μM	Present study

1. S. Shariati and G. Khayatian, *RSC Adv*., 2021, **11**, 3295. (Reference No. 34 in the main text)

2. P. Li, S. M. Lee, H. Y. Kim, S. Kim, S. Park, K. S. Park &H. G. Park *Sci Rep,*2021, **11**, 3937. (Reference No. 35 in the main text)

3. Reference no. 28 in the main text.

4. Z. Chen, Y. He, S. Luo, H. Lin, Y. Chen, P. Sheng, J. Li, B. Chen, C. Liu and Q. Cai, *Analyst***,** 2010, **135**, 1066-1069. (Reference No. 36 in the main text)

5. Reference no. 30 in the main text.

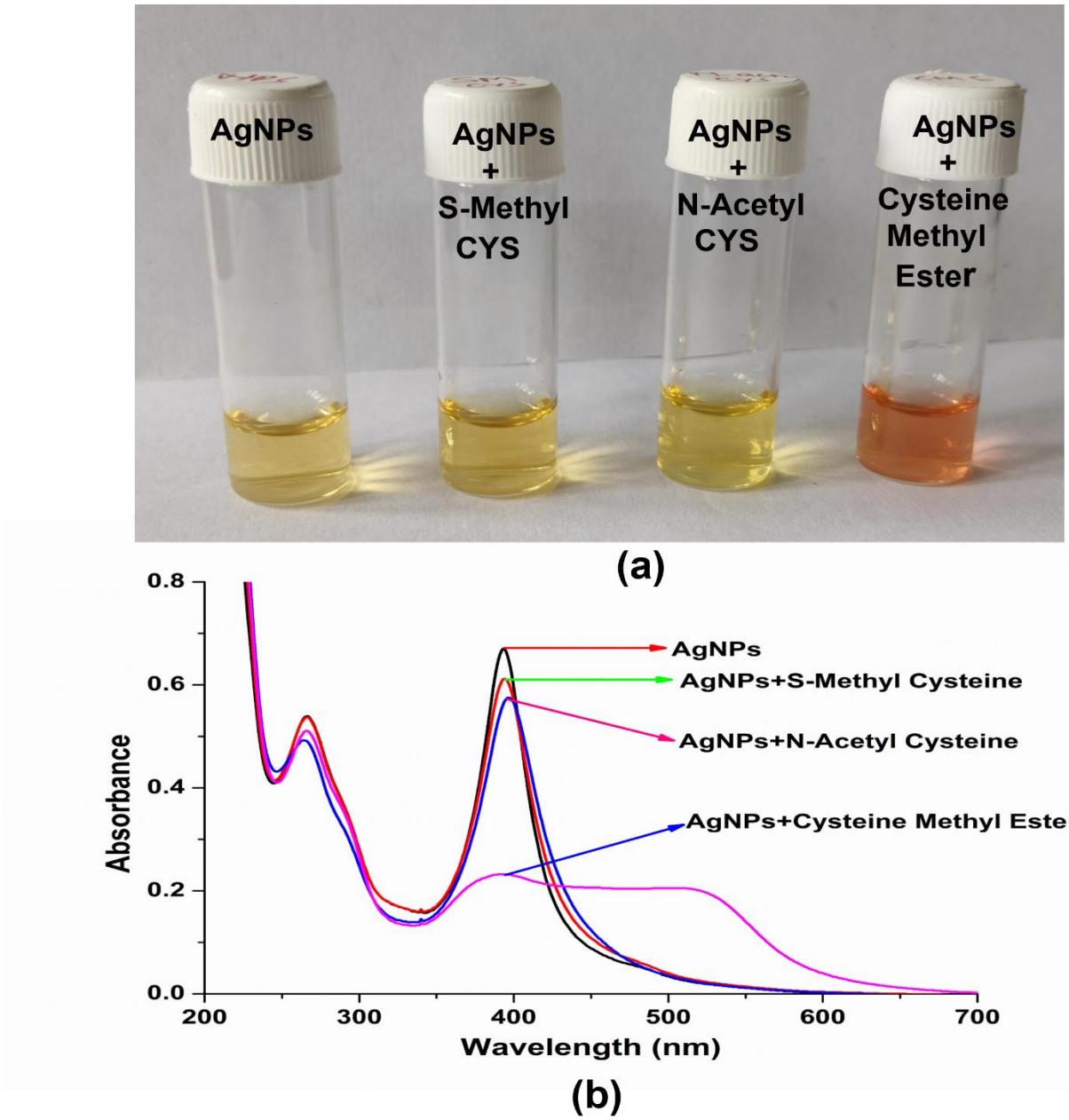


Fig.S28: Showing (a) visual and (b) UV-Visible spectral changes for the interaction of AgNPs with; (I) S-Methyl cysteine (II) N-Acetyl cysteine (III) Cysteine methyl ester.