pH-dependent discriminative detection of catecholamine neurotransmitters using 4-borono benzoic acid functionalized silver nanoparticles as a colorimetric probe.

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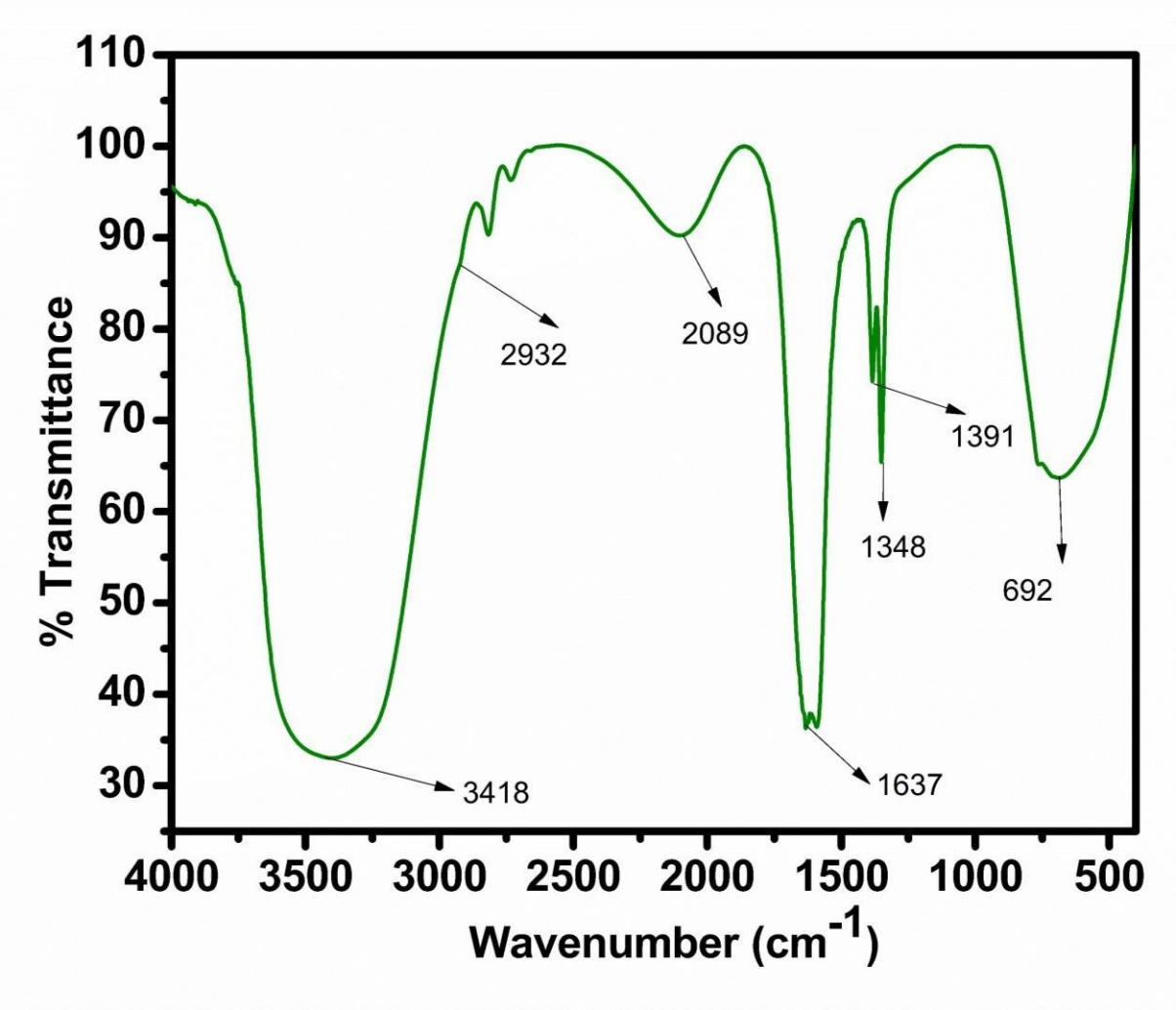


Fig. S1. FT-IR spectra of as synthesized AgNPs.

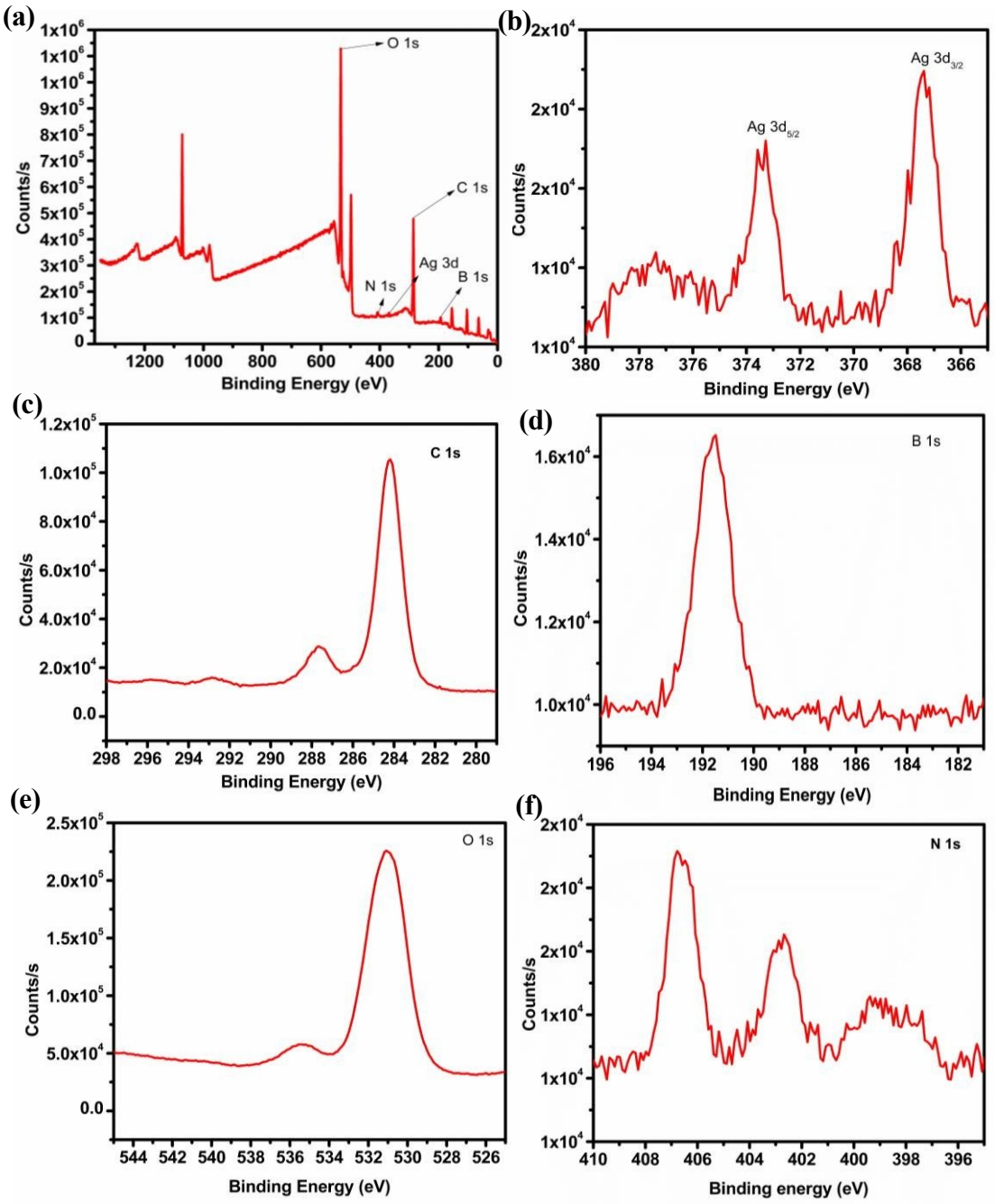


Fig. S2. XPS spectra of AgNPs. (a) XPS survey spectra. (b) High resolution Ag 3d spectra. (c**)** High resolution C 1s spectra. (d) High resolution B 1s spectra. (e) High resolution O 1s spectra. (f) High resolution N 1s spectra.

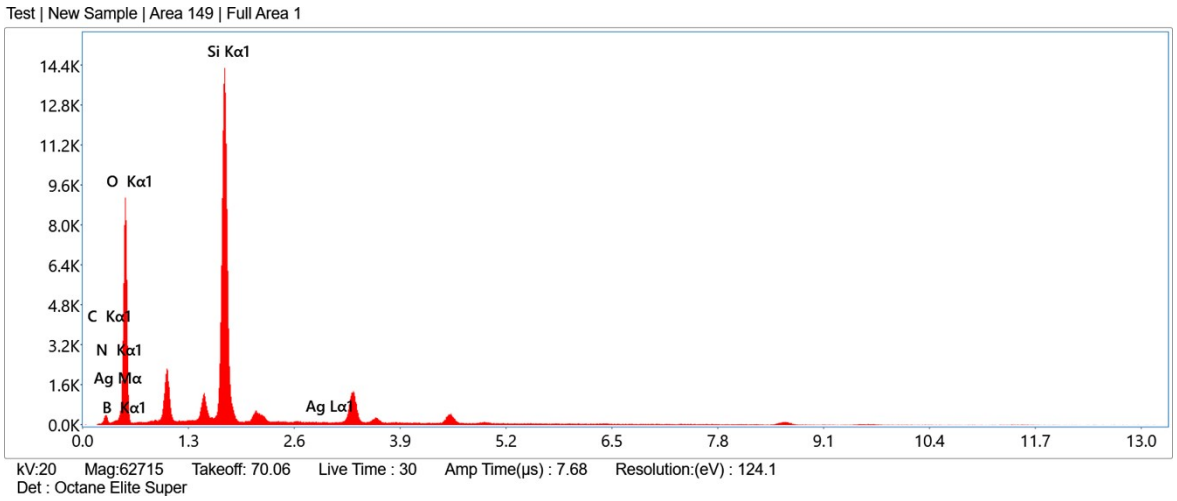


Fig. S3. EDAX spectrum of AgNPs.

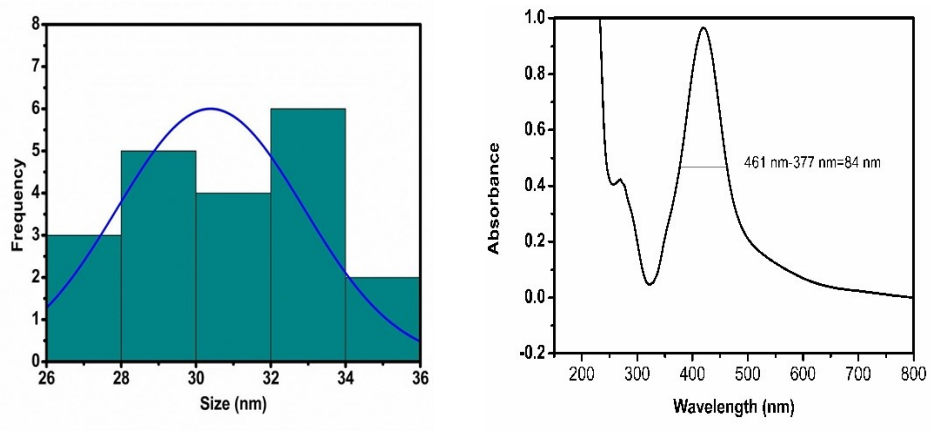


Fig. S4. (a) Histogram depicting size distribution of synthesized AgNPs, (b) PWHM of AgNPs

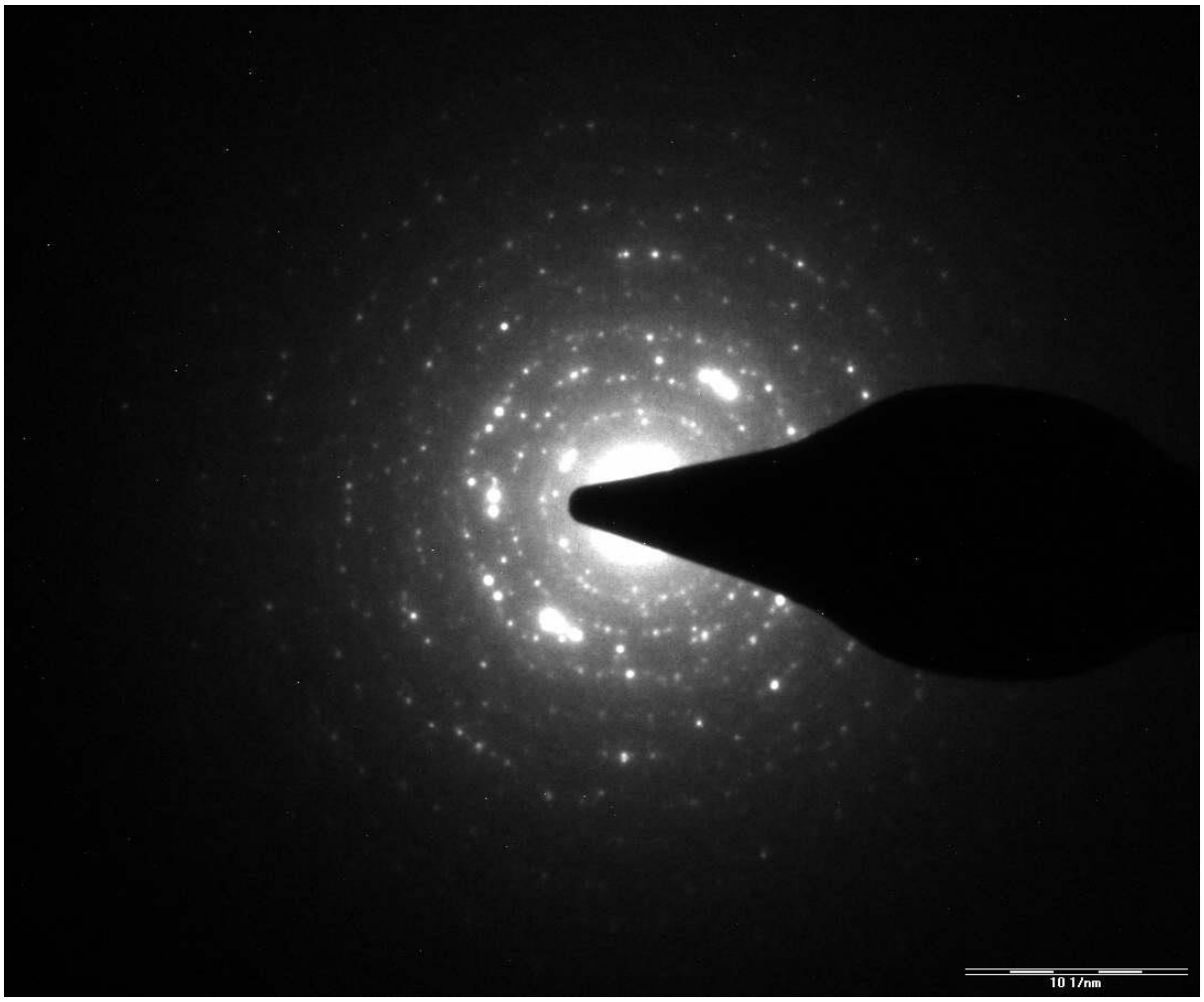


Fig. S5. SAED image of AgNPs

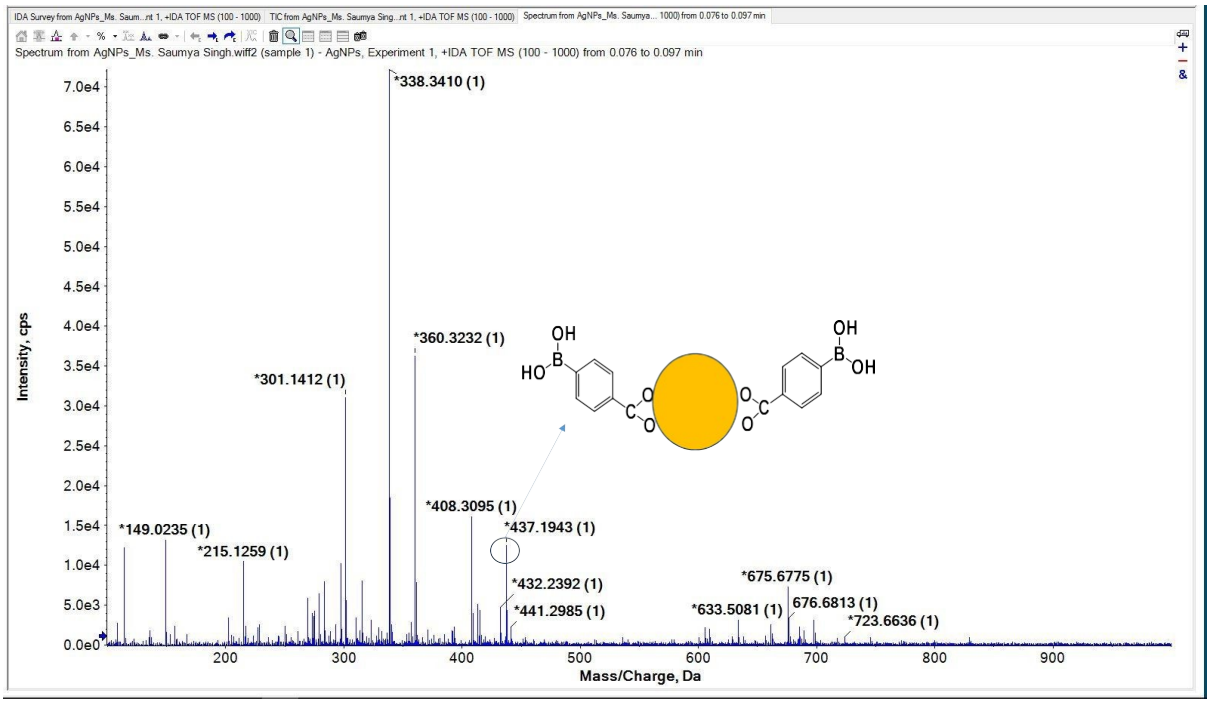
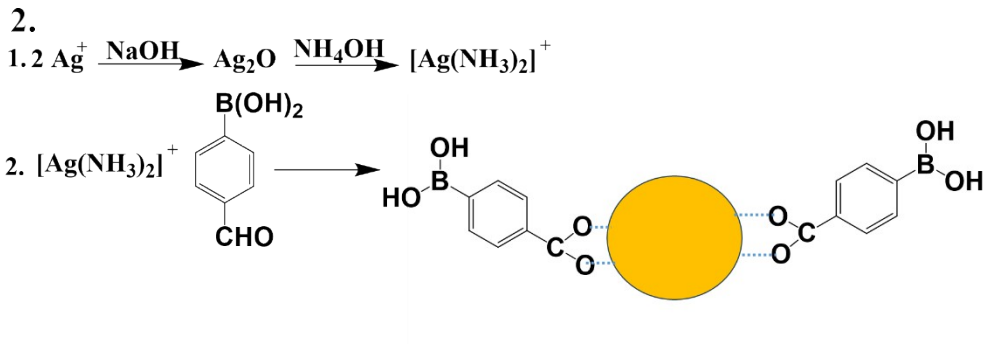


Fig. S6. HRMS of AgNPs



Scheme S1. Mechanism of synthesis of AgNPs.

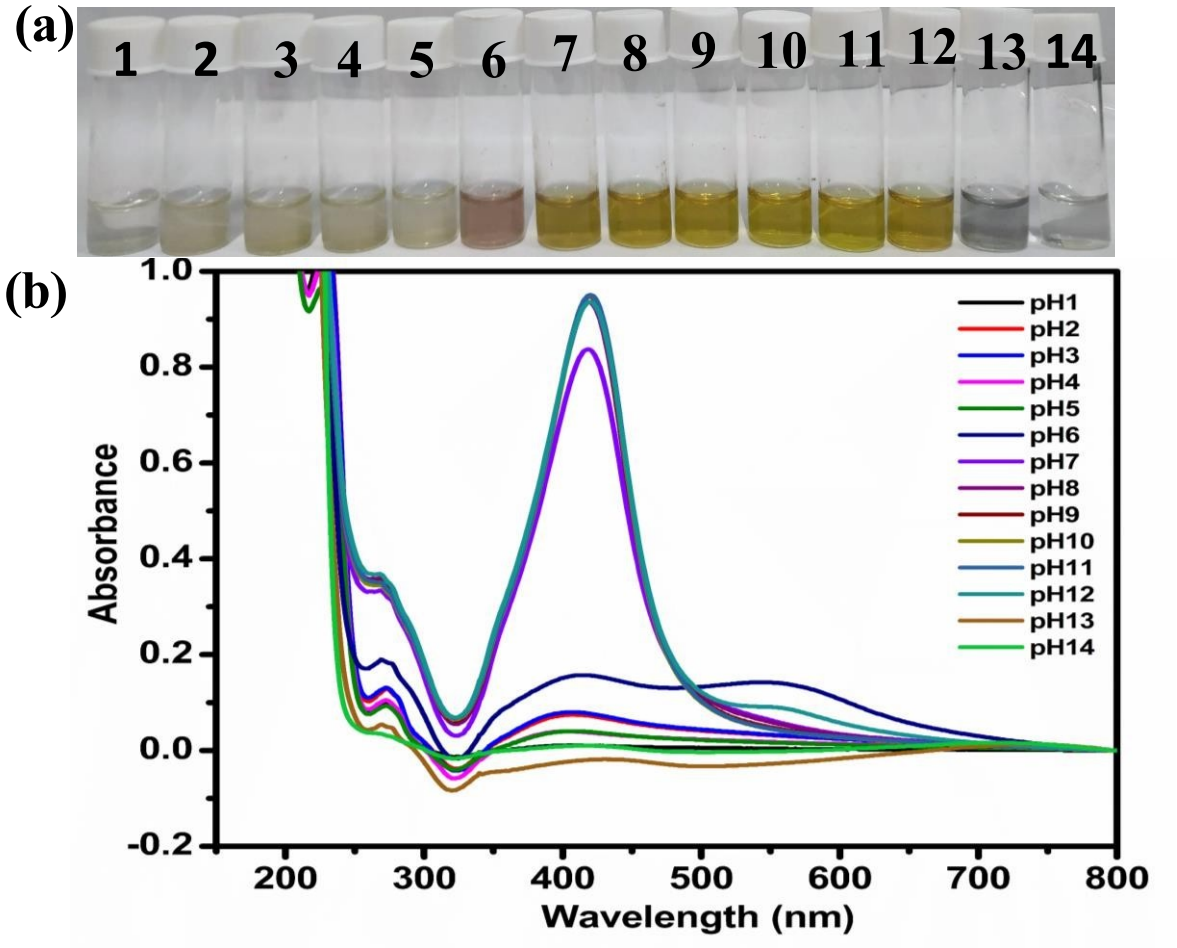


Fig. S7. (a) Visual response of AgNPs under different pH conditions. (b) UV- Vis spectra showing the effect of pH on AgNPs.

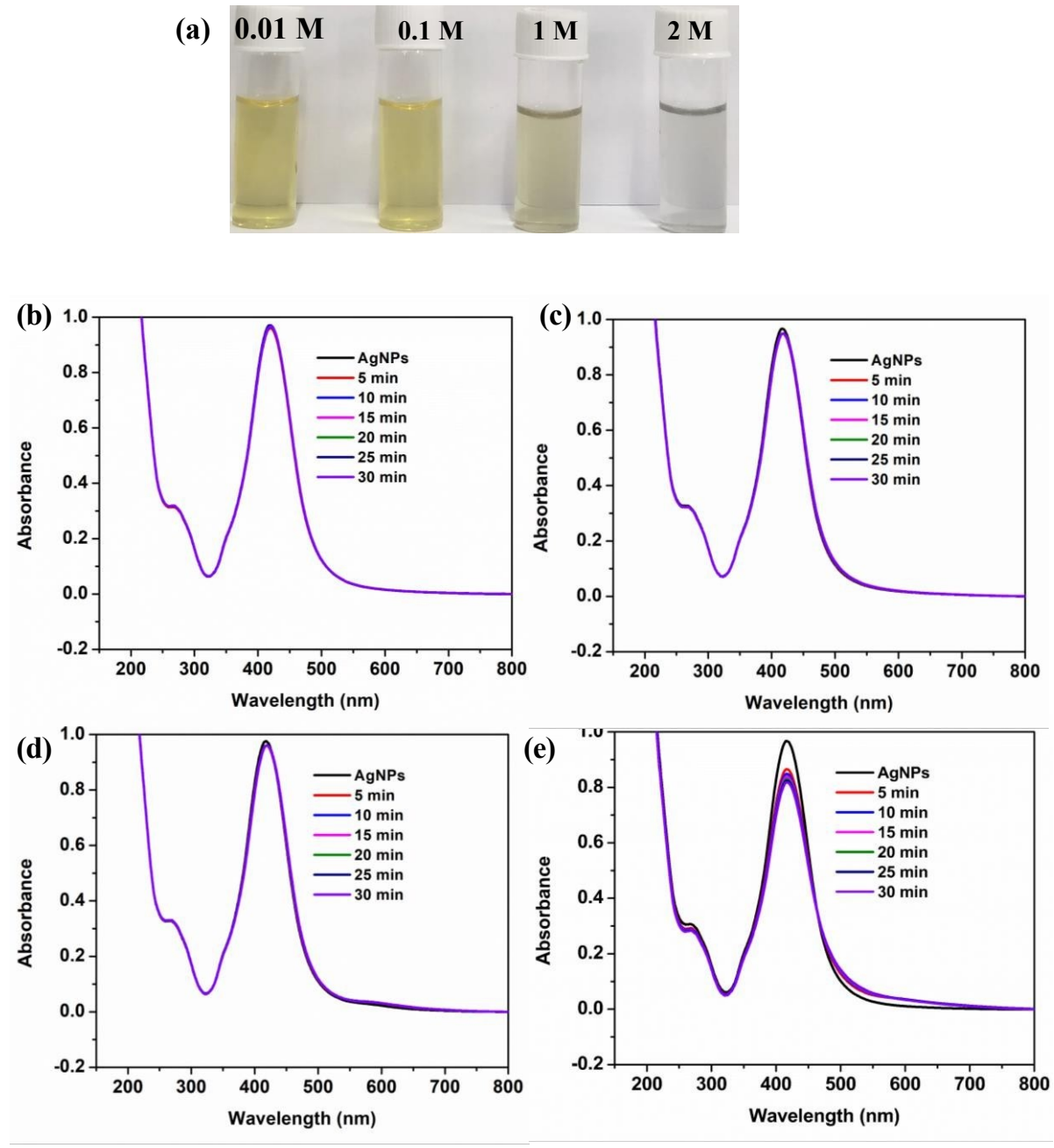


Fig. S8 (a) Visual response of AgNPs against different molar concentrations of NaCl. (b) UV-Vis spectra of AgNPs upon addition of 0.01 M NaCl. (c) UV-Vis spectra of AgNPs upon addition of 1 M NaCl. (d) UV-Vis spectra of AgNPs upon addition of 2 M NaCl.

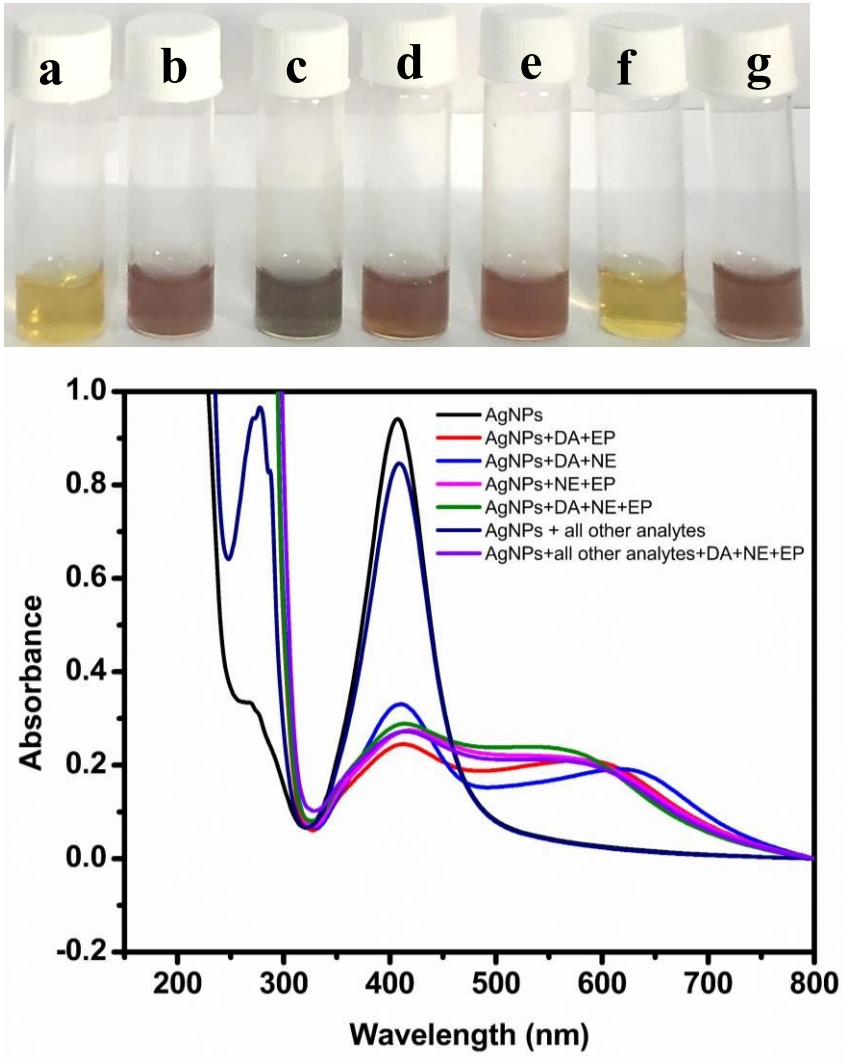


Fig. S9. Matrix studies

Table S1 Comparison between methods for the detection of DA, NE and EP.

S.No.	Method	Material	LOD	Selectivity	Reference
1.	Colorimetry	Copper-gold nanoparticles	0.142 µM	Only selective to DA	1
2	Colorimetry	Gold nanoparticles	0.09 µM	Only selective to NE	2
3	Colorimetry	Core shell gold- silver nanoparticles	0.08 µM	Only selective to DA	3
4	Colorimetry	Gold nanoparticles	0.3 µM (DA) , 0.2 µM (NE), 0.5 µM (EP)	Selective to DA, NE and EP	4
5	**Colorimetry**	**Silver nanoparticles**	**92 nM (DA) 93 nM (NE) 97 nM (EP)**	**Selective to DA , NE and EP**	**This work**

References

1. Sun, Y., Peng, M., Wu, A., & Zhang, Y. (2023). Multicolor colorimetric detection of dopamine based on iodide-responsive copper–gold nanoparticles. *Chemical Communications*, *59*(81), 12180-12183.
2. Godoy-Reyes, T. M., Costero, A. M., Gavina, P., Martinez-Manez, R., & Sancenon, F. (2019). A colorimetric probe for the selective detection of norepinephrine based on a double molecular recognition with functionalized gold nanoparticles. *ACS Applied Nano Materials*, *2*(3), 1367-1373.
3. Le, T. V., & Lee, S. W. (2022). Core–shell Au–Ag nanoparticles as colorimetric sensing probes for highly selective detection of a dopamine neurotransmitter under different pH conditions. *Dalton Transactions*, *51*(41), 15675-15685.
4. Hassani-Marand, M., Fahimi-Kashani, N., & Hormozi-Nezhad, M. R. (2023). Machine-learning assisted multiplex detection of catecholamine neurotransmitters with a colorimetric sensor array. *Analytical Methods*, *15*(9), 1123-1134.

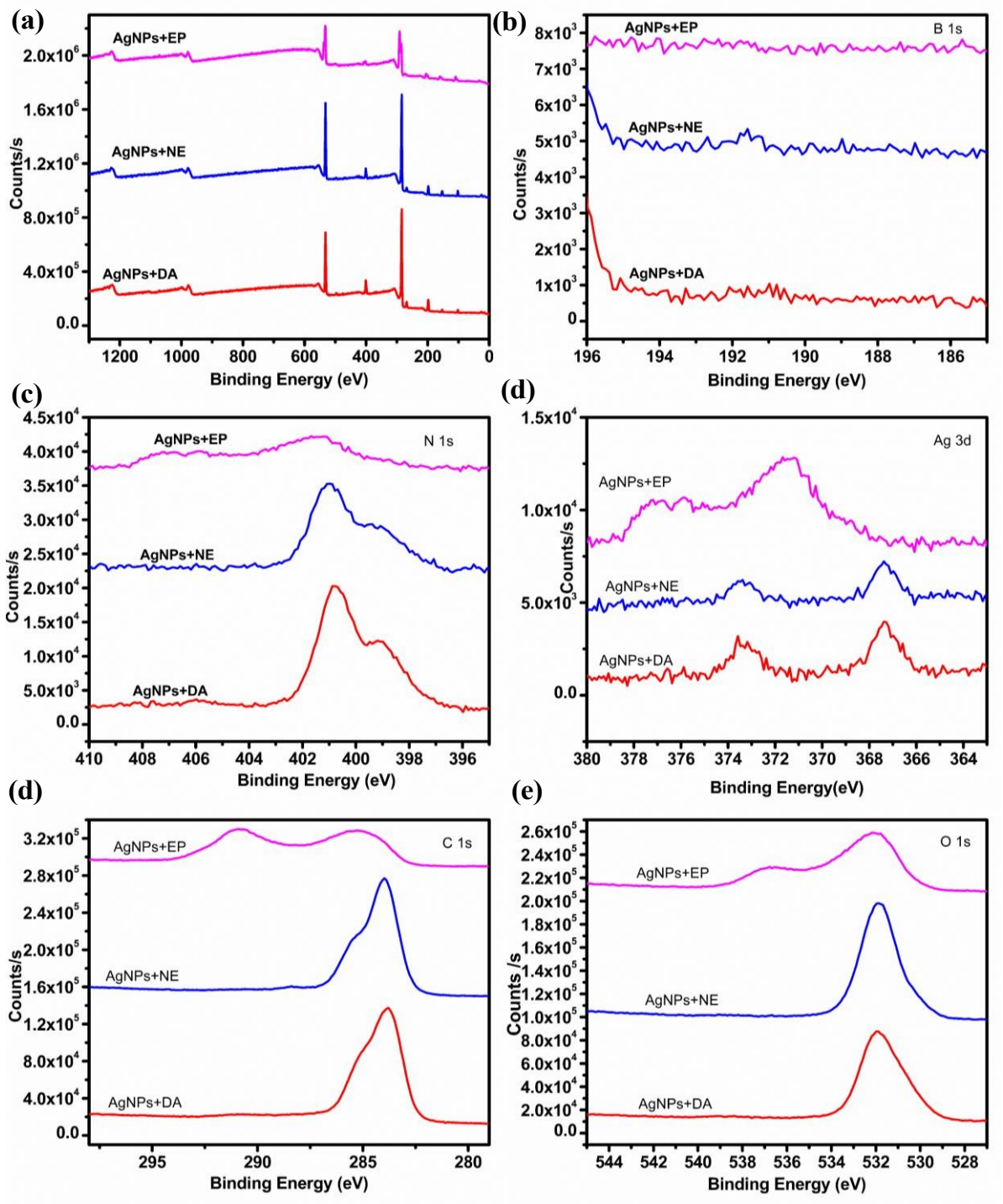


Fig. S10. XPS spectra of AgNPs after the addition of DA, NE and EP. (a) XPS survey spectra. (b) High resolution Ag 3d spectra. (c**)** High resolution C 1s spectra, (d) High resolution B 1s spectra. (e) High resolution O 1s spectra. (f) High resolution N 1s spectra.

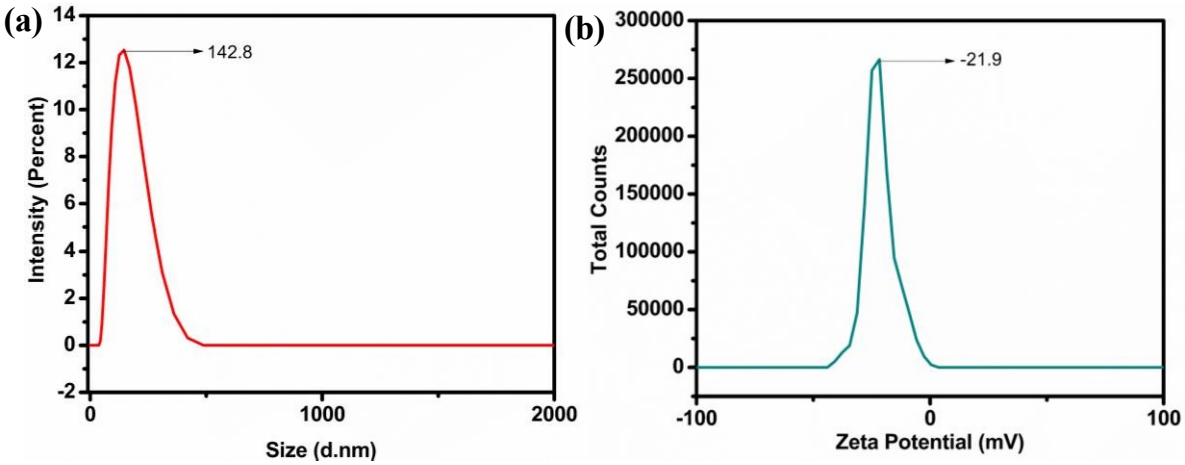


Fig. S11. DLS and zeta potential studies after the addition of DA into AgNPs.

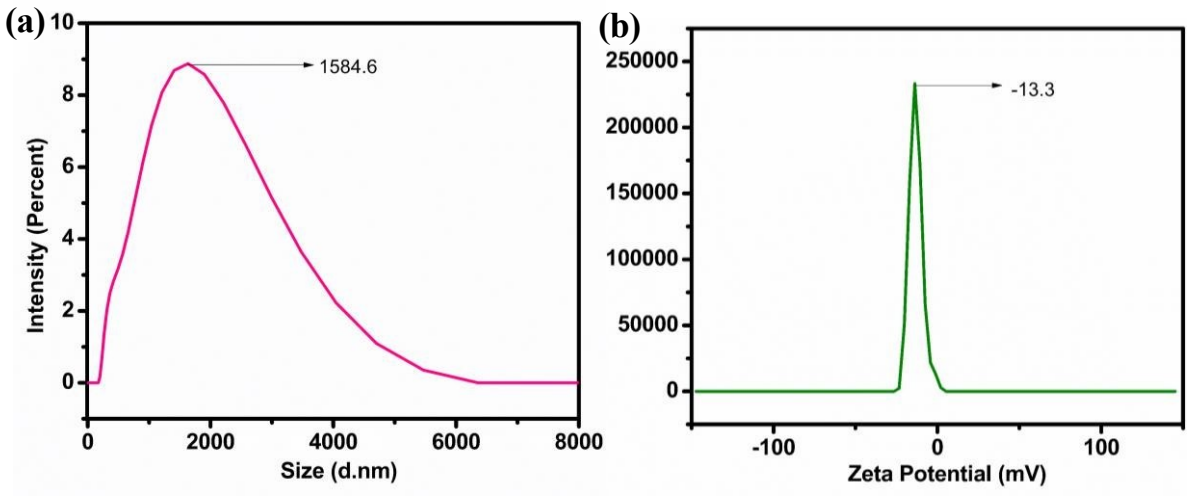


Fig. S12. DLS and zeta potential studies after the addition of NE into AgNPs.

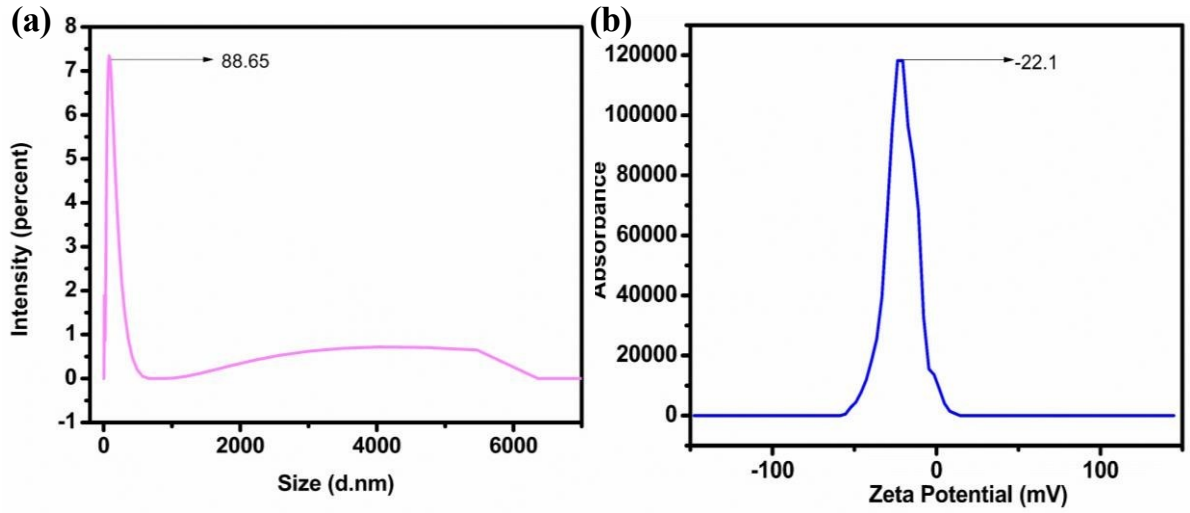
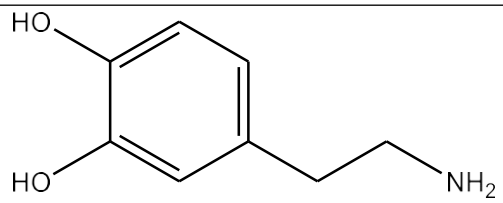
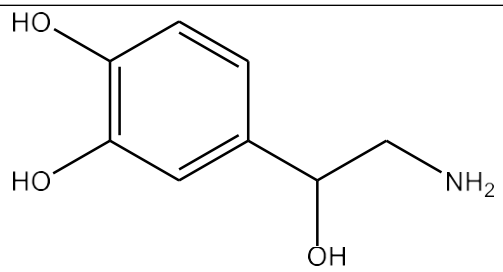
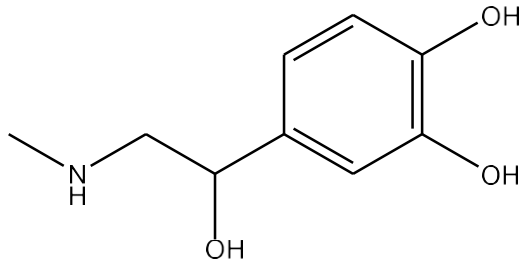


Fig. S13 DLS and zeta potential studies after the addition of EP into AgNPs

Table 2 Structures of neurotransmitters DA, NE and EP with their pKa values

S.No.	Structure	pKa values
1	 dopamine	$pKa_{1=}$ 9.4 $pKa_{2=}$ 10.8 $pKa_{3=}$12.8
2	 norepinephrine	$pKa_{1=}$8.6 $pKa_{2=}$9.8 $pKa_{3=}$ 12.0
3	 epinephrine	$pKa_{1=}$8.6 $pKa_{2=}$8.8 $pKa_{3=}$10.0

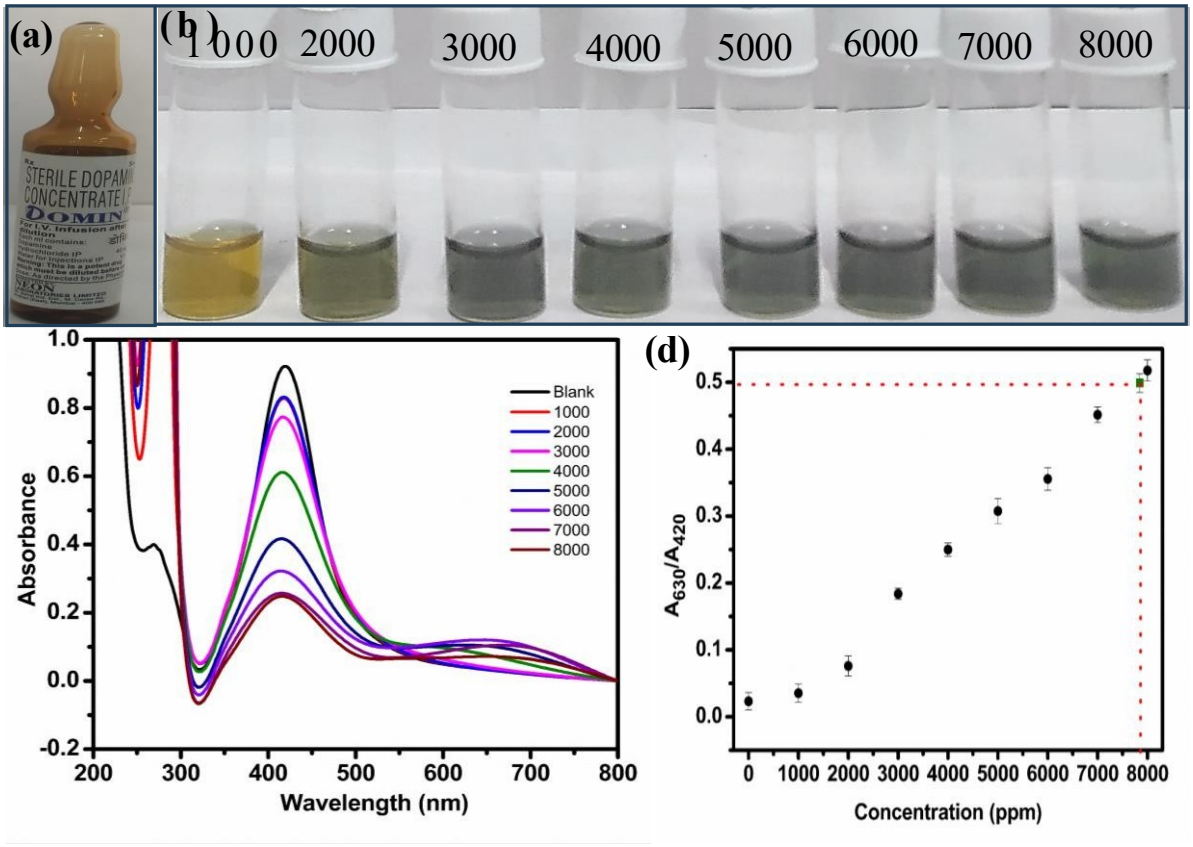


Fig. S14. Photograph of dopamine hydrochloride injection (Domin). (b) Visual response upon addition of DA hydrochloride injections from 10000 ppm to 80000 ppm into AgNPs. (c) Calibration plot for the detection of DA in real samples

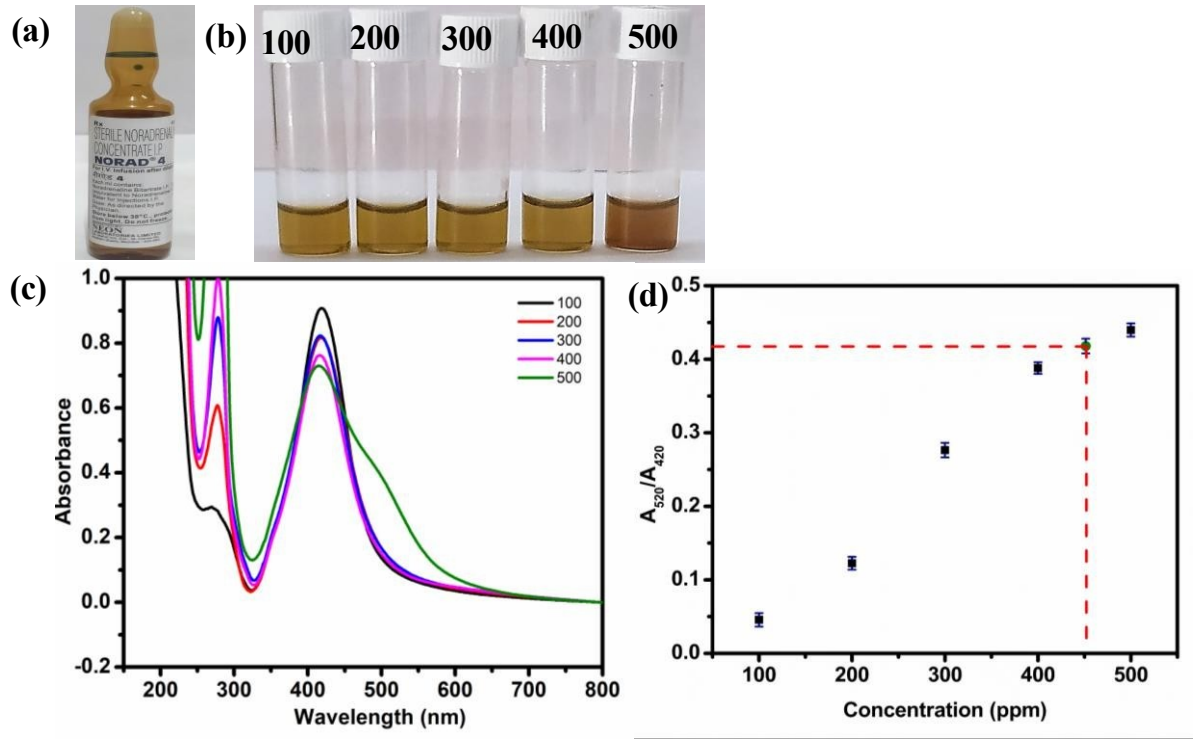


Fig. S15. (a) Photograph of norepinephrine hydrochloride injection (Norad). (b) Visual response upon addition of NE hydrochloride injections from 100 ppm to 500 ppm into AgNPs. (c) Calibration plot for the detection of NE in real samples.

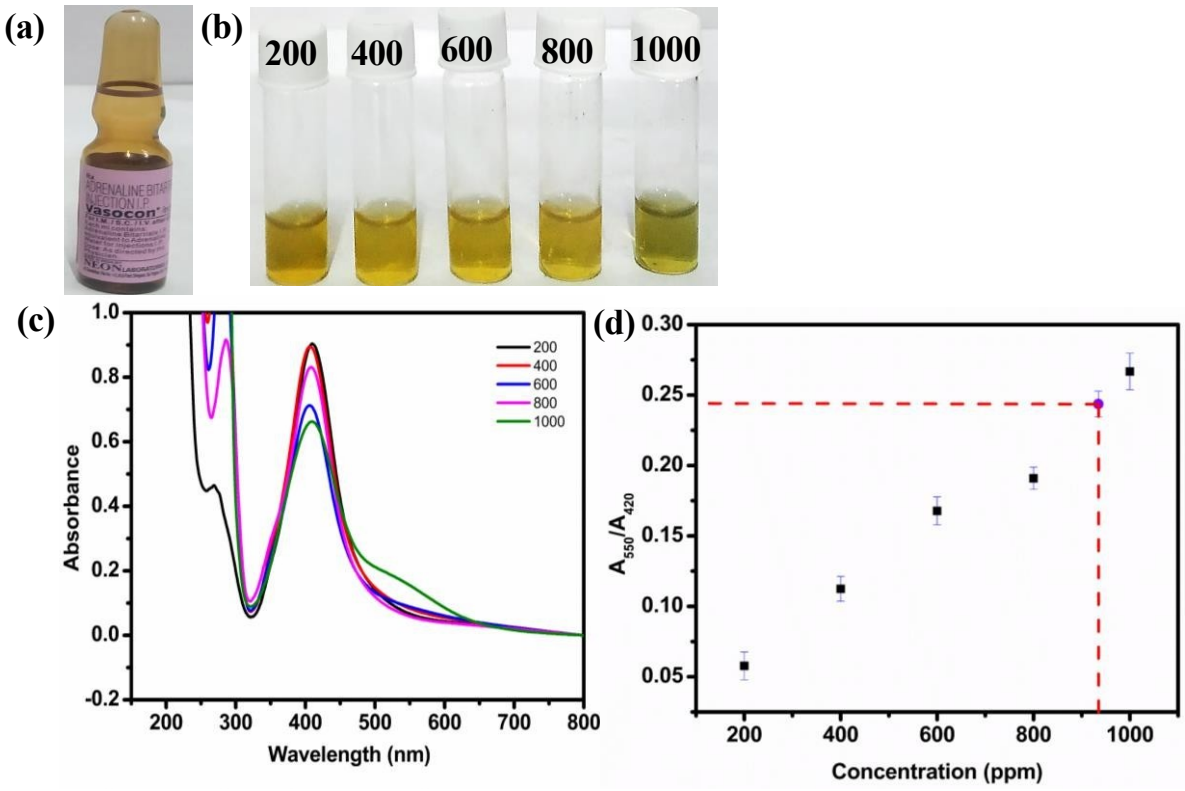
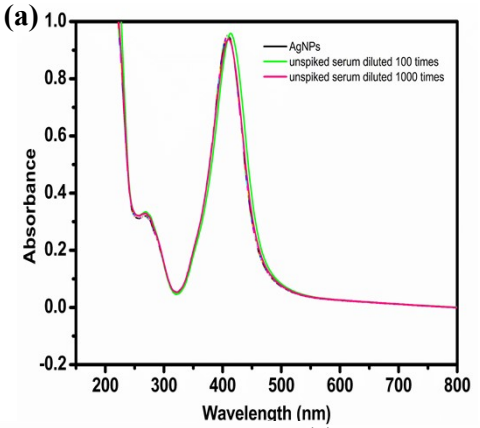
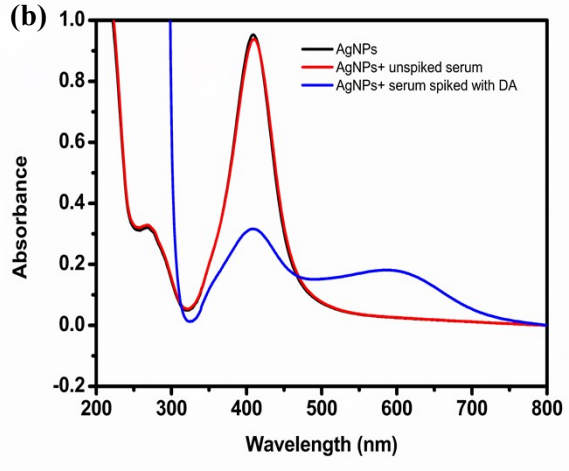
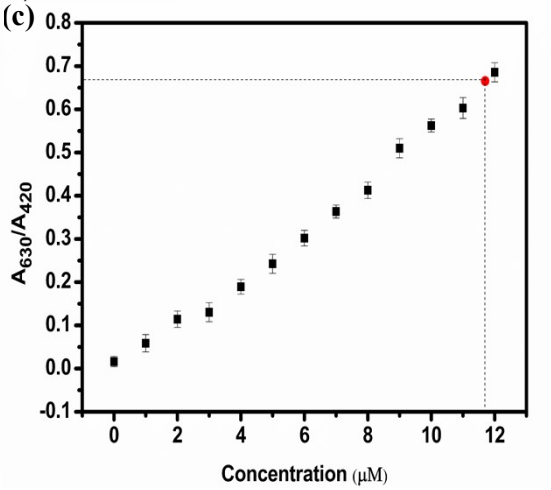
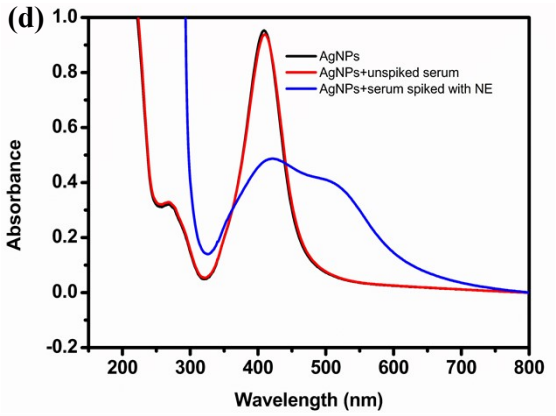


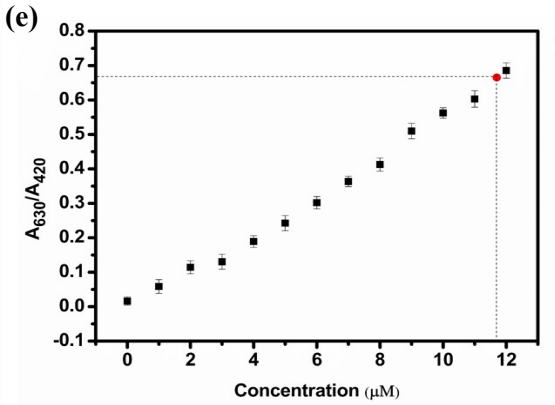
Fig. S16. (a) Photograph of epinephrine hydrochloride injection (Adrenalin). (b) Visual response upon addition of EP hydrochloride injections from 200 ppm to 1000 ppm into AgNPs. (c) Calibration plot for the detection of EP in real samples

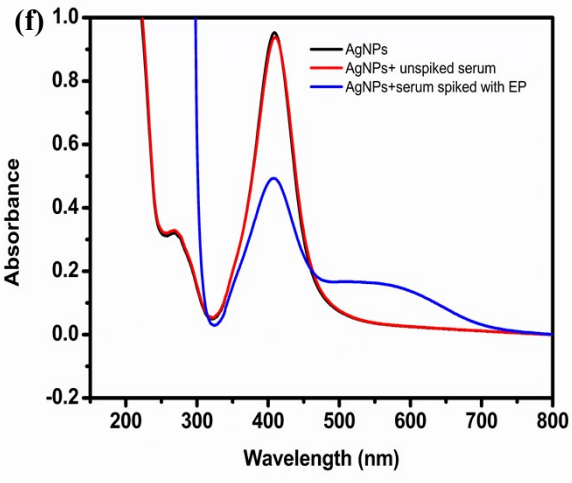

(a)
AgNPs
unspiked serum diluted 100 times
unspiked serum diluted 1000 times
Absorbance
Wavelength (nm)


(b)
AgNPs
AgNPs+ unspiked serum
AgNPs+ serum spiked with DA
Absorbance
Wavelength (nm)


(c)
A630/A420
Concentration (μM)


(d)
AgNPs
AgNPs+unspiked serum
AgNPs+serum spiked with NE
Absorbance
Wavelength (nm)


(e)
A630/A420
Concentration (μM)


(f)
AgNPs
AgNPs+ unspiked serum
AgNPs+serum spiked with EP
Absorbance
Wavelength (nm)

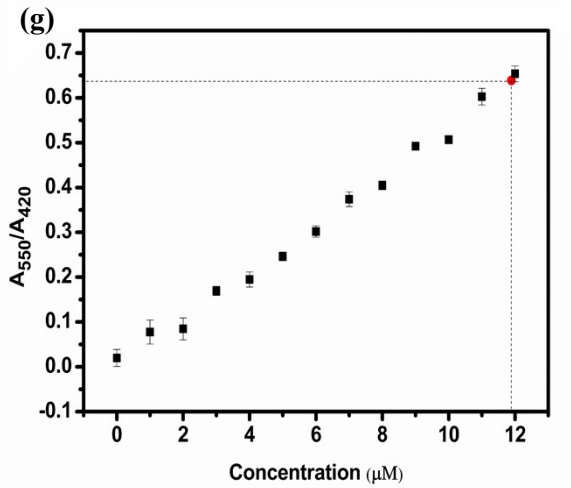

(g)
A550/A420
Concentration (μM)

Fig. S17 (a) UV-Vis spectra of AgNPs, blood serum (diluted 100 times), blood serum (diluted 1000 times) (b,c) UV Vis spectral studies of serum spiked with DA and corresponding calibration plot for determination of recovery. (d,e) UV-Vis spectral studies of serum spiked with NE and corresponding calibration plot for the determination of recovery. (e,f) UV-Vis spectral studies of serum spiked with EP and corresponding calibration plot for the determination of recovery.

Concentration of spherical silver nanoparticles (AgNPs) can be determined by using the equation C= where N_{Total}/NVN_A where N_{Total} is the total number of silver atoms in the reaction solution, N is the number of silver atoms present in each nanoparticle, V is volume of solution in litres and N_A is Avogadro constant. Herein, we have used 4mL of 4mM $AgNO_3$ in a total volume of 50mL.

N=31 d^3 = $31\times (33)^3 = 1{,}114{,}047$

Concentration of AgNPs = $\frac{N_{Total}}{NVN_A}$

$= \frac{0.016\times10^{-3}\times6.02\times10^{23}}{1{,}114{,}047 \times 0.05\times6.02\times10^{23}}$

$= 2.9\times10^{-10}$ M

0.29 nM