Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

Core-shell Au-Ag nanoparticles as colorimetric sensing probes for highly selective detection of dopamine neurotransmitter under different pH conditions

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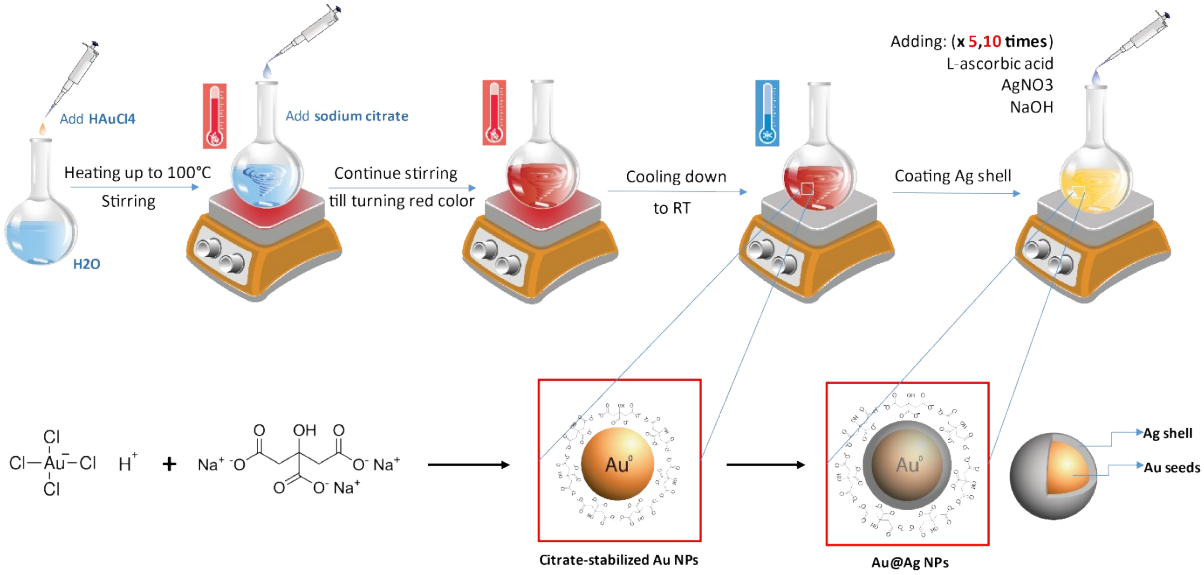


Scheme S1. Synthesis of core-shell Au@Ag NPs with different Ag shell thicknesses.

Table S1. Comparison between colorimetric DA-detection methods

Sensing Materials	**Synthesis method**	**LOD (Linear range)**	**Selectivity to other catecholamine at different pH condition**	**Time**	**Ref.**
Pt/hBNNSs	Decoration of the boron nitride nanosheets with Pt NPs	0.76 μM (2-55 μM)	No selectivity comparison of DA with norepinephrine and epinephrine at pH 4	20 min	[1]
Cu^{2+} / oxTMB system	Catalyzing the TMB oxidation by Cu^{2+}	1.00 μM (1-50 μM)	No selectivity comparison of DA with norepinephrine and epinephrine at pH 4	10 min	[2]
Pt/CoSn(OH)$_6$	Catalyzing the TMB oxidation by Pt/CoSn(OH)$_6$	0.76 μM (5-60 μM)	No selectivity comparison of DA with norepinephrine and epinephrine at pH 4	3 min	[3]
Fe_3O_4 NPs	Ethanediol-based solvothermal synthesis	3.50 nM (0.01-4 μM)	No selectivity comparison of DA with norepinephrine and epinephrine at pH 3.0	20 min	[4]
NiCo2S$_4$-rGO	Hydrothermal synthesis	0.42 μM (0.5-100 μM)	No selectivity comparison of DA with norepinephrine and epinephrine at pH 4	15 min	[5]
Au NPs	$NaBH_4$ reduction in the presence of CTAB	0.033 μM (0-1 μM)	No selectivity comparison of DA with norepinephrine and epinephrine at pH 13	20 min	[6]
Au@Ag NPs	Disproportionation reaction of Au^{3+}, Ag^{-}	0.08 μM (0-25 μM)	**High selectivity of DA against epinephrine and norepinephrine at pH 10**	25 min	**This study**

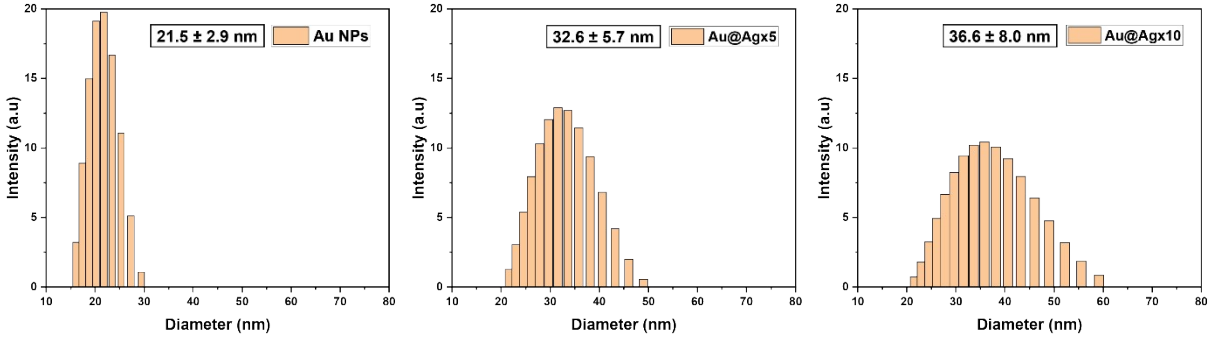
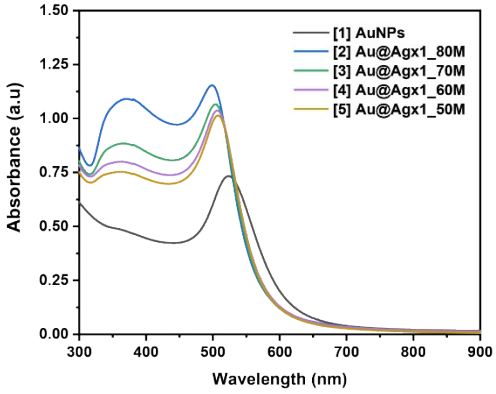
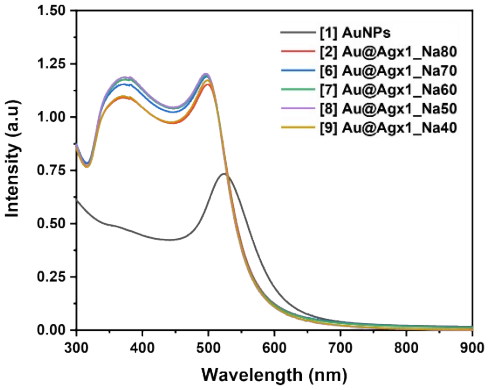


Fig. S1. DLS size distribution of Au NPs, Au@Agx5, Au@Agx10



No.	ID	AA (60µL)	NaOH (60µL)	AgNO3 (15µL)	No. of Ag^+ addition	Size of Au@Ag
1	AuNPs	0	0	0	0 times	**29.3** ± 4.5
2	AuAgx1_80M	80mM	80mM	80mM	1 times	**37.5** ± 6.8
3	AuAgx1_70M	70mM	80mM	70mM	1 times	**32.1** ± 6.5
4	AuAgx1_60M	60mM	80mM	60mM	1 times	**31.0** ± 5.4
5	AuAgx1_50M	50mM	80mM	50mM	1 times	**31.7** ±4 .9

Fig. S2. The UV-vis spectra of Au@Ag NPs solution after 1st reduction with different concentrations of reaction reagents in the synthesis of core-shell Au@Ag NPs. Note: The inserted Table shows the survey of the concentration effects of $AgNO_3$ and NaOH on the reduction process of silver shell with the size of NPs.



No.	ID	AA (60μL)	NaOH (60μL)	AgNO3 (15μL)	No. of Ag^+ addition	Size of Au@Ag
2	AuAgx1_80M	80mM	80mM	80mM	1 times	**37.5** ± 6.8
6	AuAgx1_Na70M	80mM	70mM	80mM	1 times	**38.1** ± 7.4
7	AuAgx1_Na60M	80mM	60mM	80mM	1 times	**35.1** ± 5.6
8	AuAgx1_Na50M	80mM	50mM	80mM	1 times	**33.3** ± 11.5
9	AuAgx1_Na40M	80mM	40mM	80mM	1 times	**34.1** ± 5.1

Fig. S3. The UV-vis spectra of Au@Ag NPs solution after 1st reduction with different concentrations of reaction reagents in the synthesis of core-shell Au@Ag NPs. Note: The inserted Table shows the survey of the concentration effects of $AgNO_3$ and NaOH on the reduction process of silver shell with the size of NPs.

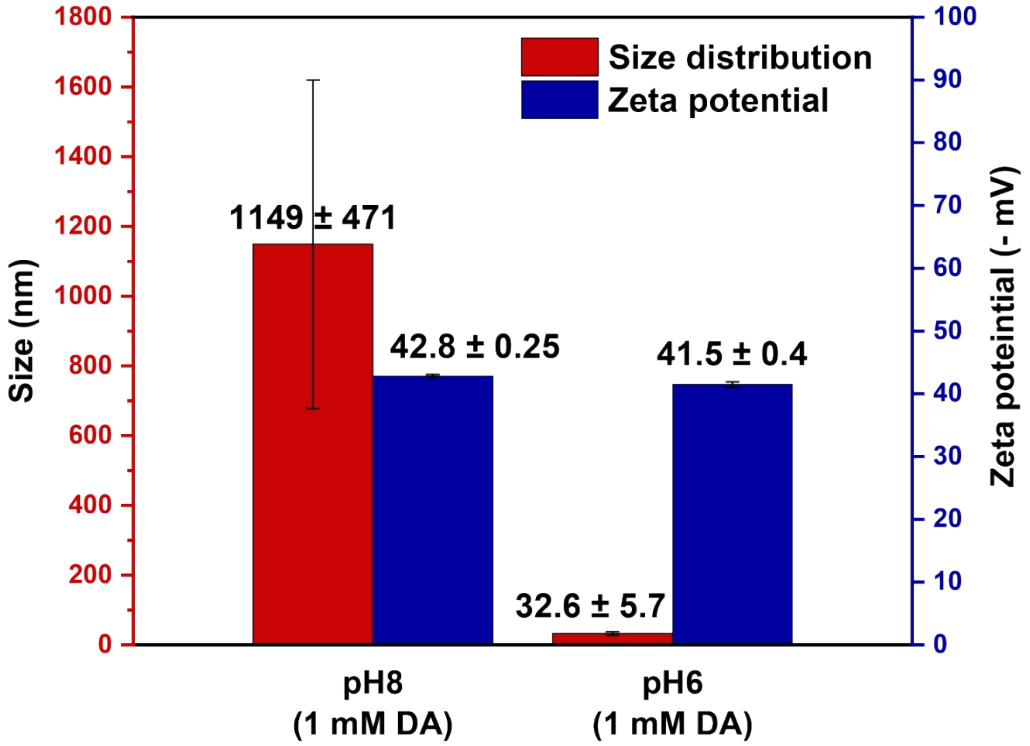


Fig. S4. The comparison of average size and zeta potentials of Au@Agx5 NPs solution at pH 6 and pH 8 in the presence of DA (1 mM), respectively. The red and blue bars indicate the particle size and zeta potentials, respectively.

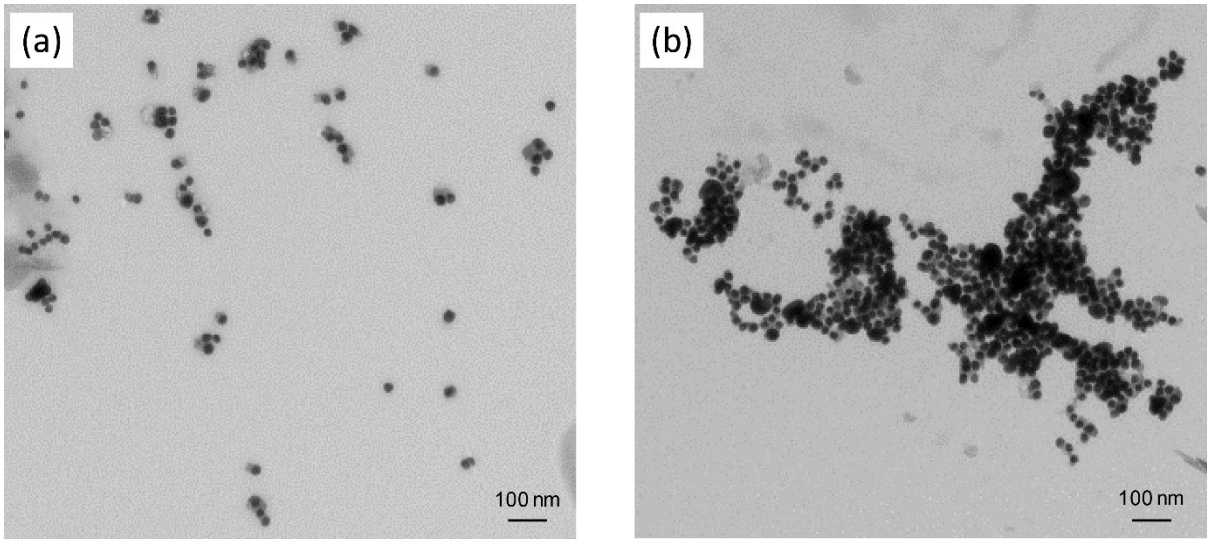


Fig. S5. TEM images of Au@Agx5 NPs in the absence (a), and presence of DA (500 μM) (b).

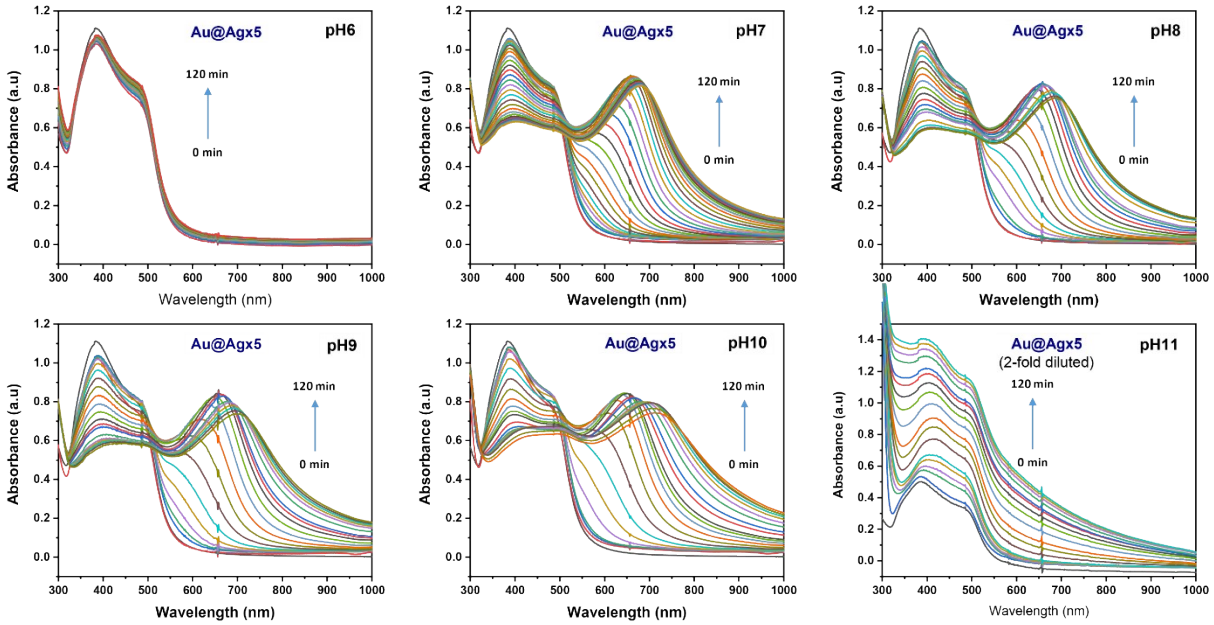


Fig. S6. UV-vis spectra of Au@Agx5 NPs solution after DA (1 mM) addition over 120 min at different pH 6-11.

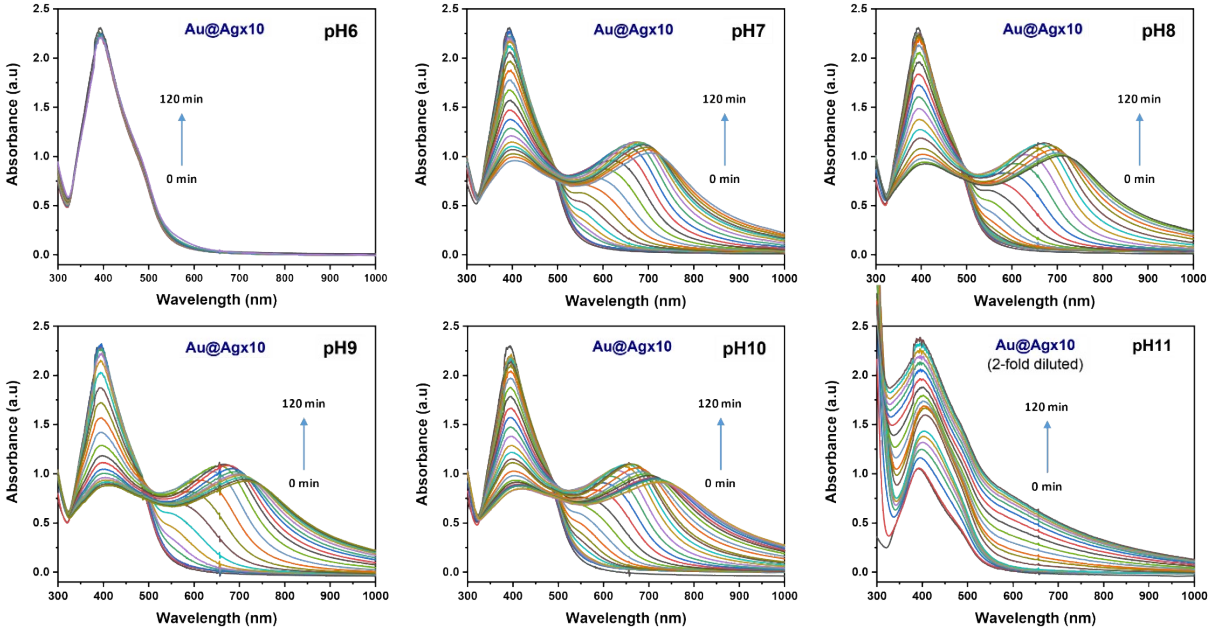


Fig. S7. UV-vis spectra of Au@Agx10 NPs solution after DA (1 mM) addition over 120 min at different pH 6-11.

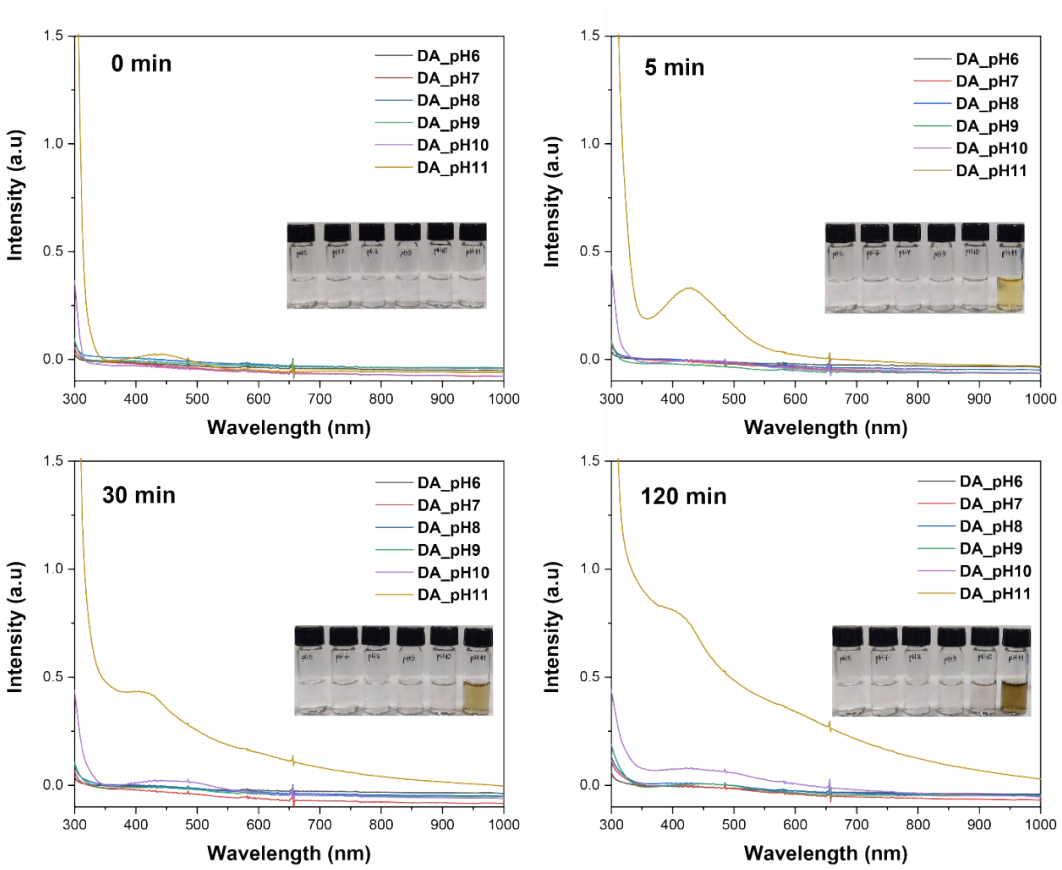


Fig. S8. The effect of pH on the color of dopamine solution (1 mM) without Au@Ag NPs.

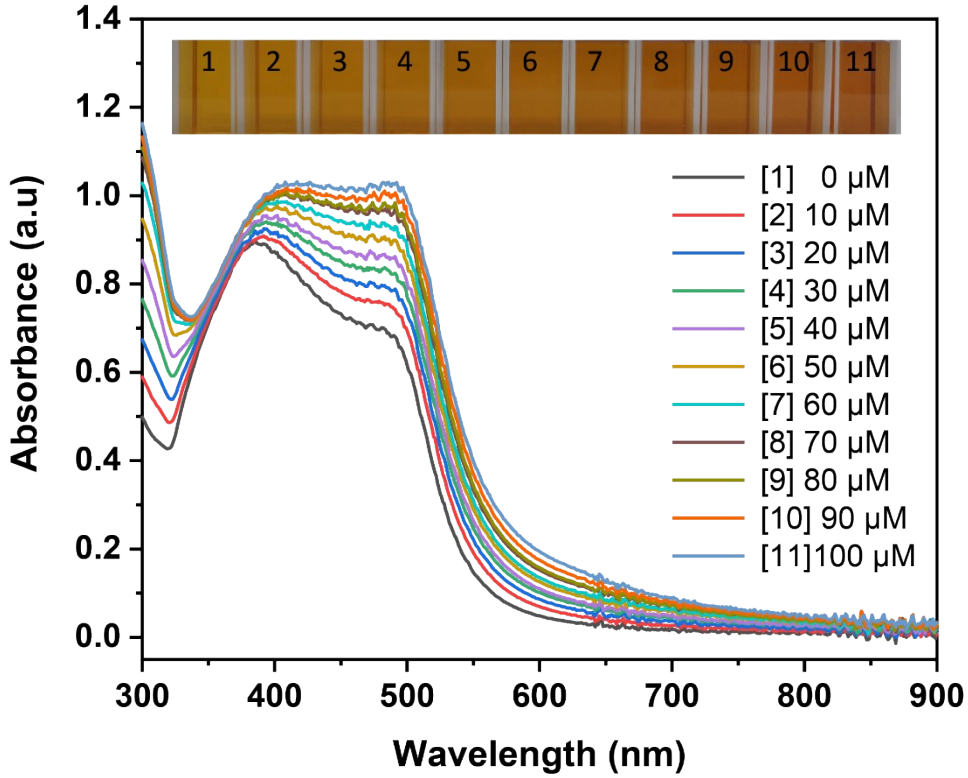


Fig. S9. Color transition and UV-vis spectra changes of Au@Agx5 NPs solution by the addition of DA at surveyed concentrations (0 - 100 μM)

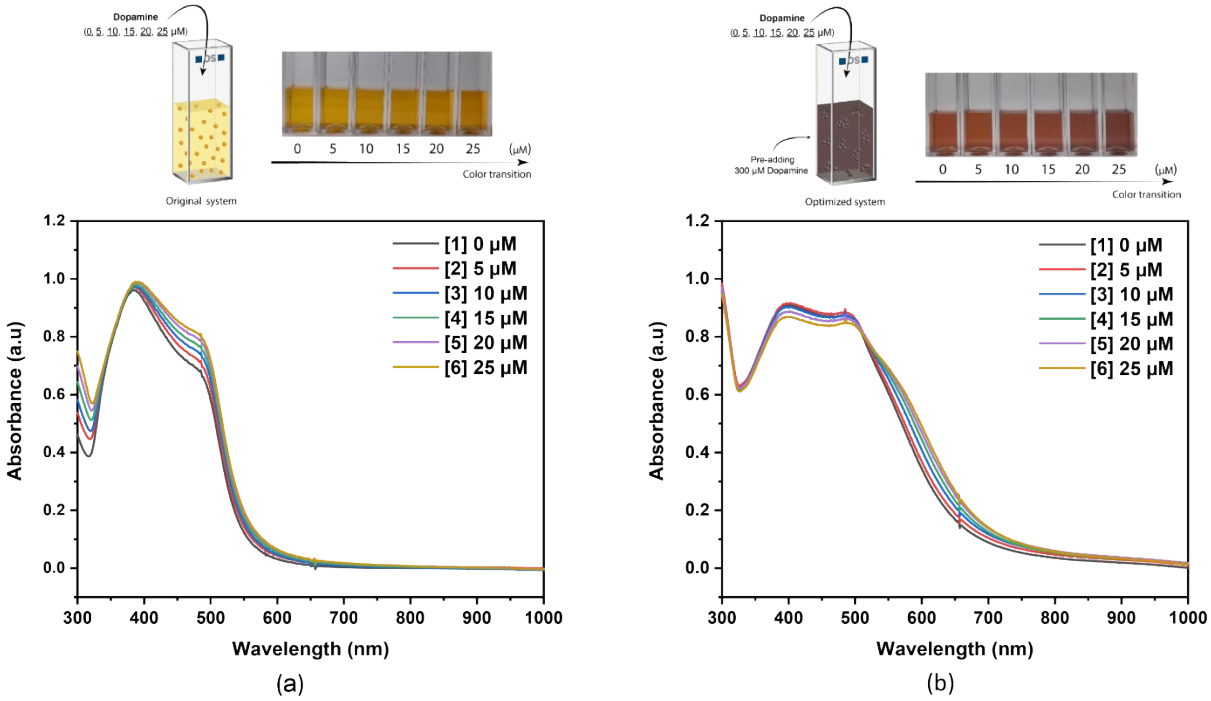


Fig. S10. UV-vis spectra changes of Au@Agx5 NPs solution at pH 10 by the addition of DA at surveyed concentrations (0–25 μM) before optimization (a), and after optimization by pre-adding 300 μM DA (b)

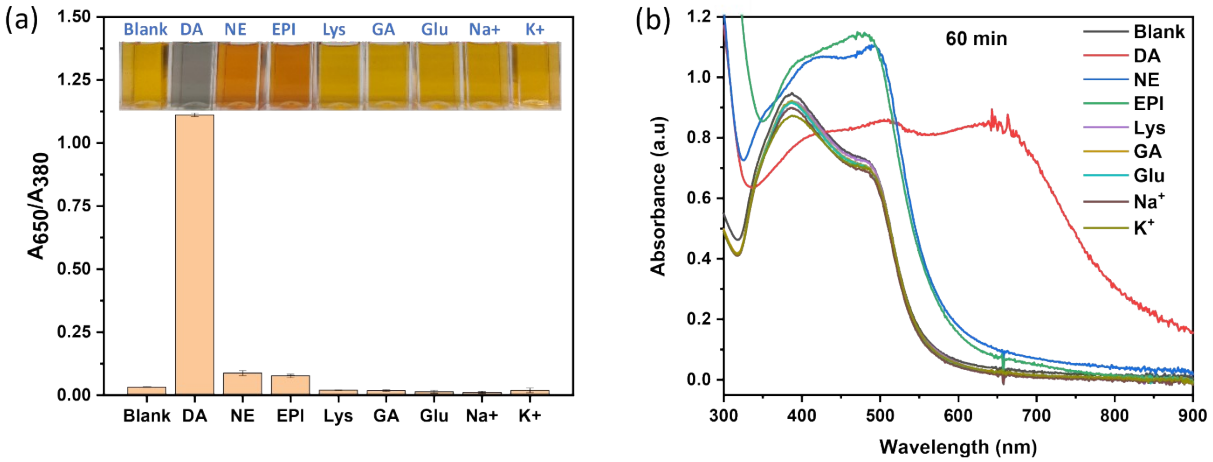


Fig. S11. UV-vis and colorimetric response of Au@Agx5 NPs solution at pH 10 within 60 min: (a) The UV-vis spectra of the NPs solution in the presence of catecholamines (DA, NE, EPI), amino acids (Lys, GA, Glu), and some mental ions (Na^+, K^+) at 500 μM of each component, (b) Absorbance ratio of A650/A380 and color variants of the NPs solution corresponding to interfering components including DA.

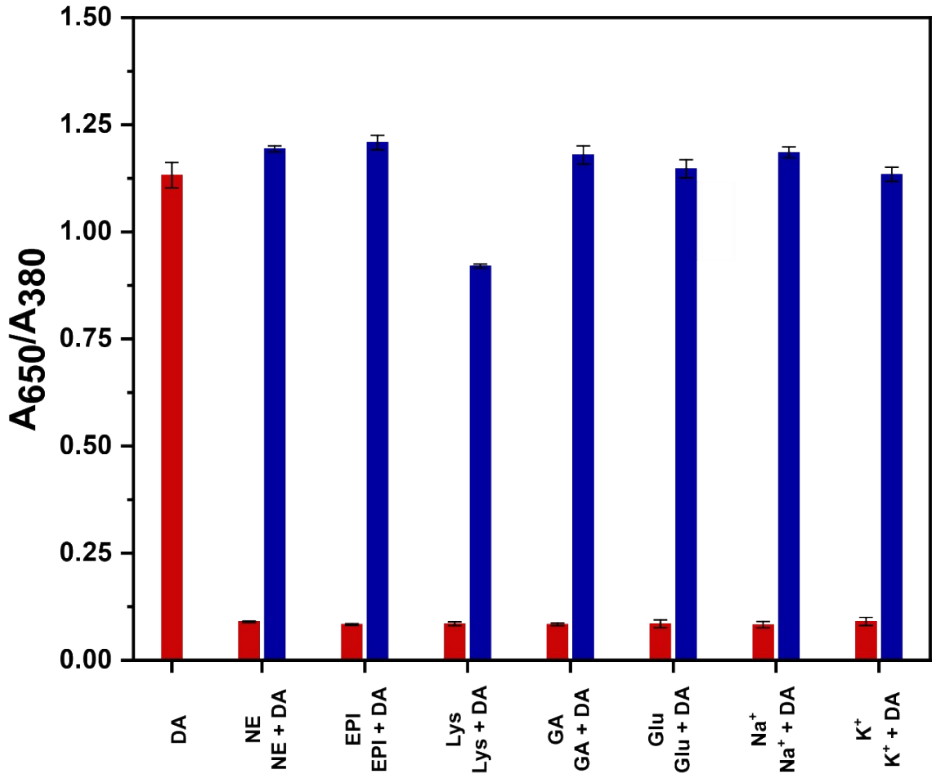
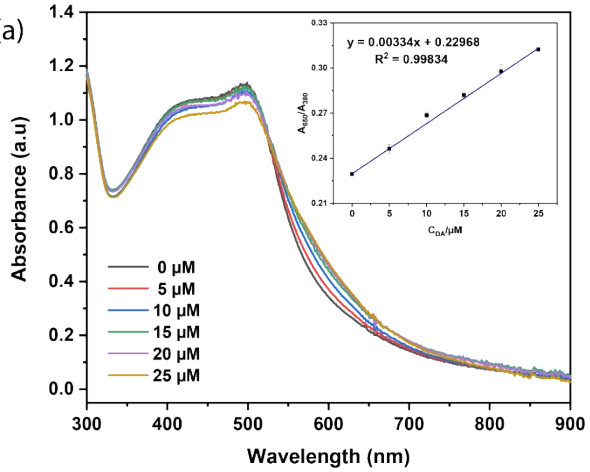


Fig. S12. The absorption ratio of A650/A380 of the Au@Agx5 NPs solution containing the mixture of DA and differently selected interfering component. The concentration of all the substances are fixed as 500 μM.

(a)



(b)

Known concentration (μM)	Found concentration (μM)	Recovery [a] (%)	RSD [b] (%)
15	18.39	122.6 %	3.0 %
20	21.63	108.15 %	4.0 %
25	24.62	98.48 %	0.9 %

(a) % recovery (found concentration/know concentration) x 10

(b) Relative Standard Deviation (n=3)

Fig. S13. (a) UV-vis spectra of Au@Agx5 NPs solution at pH 10 for the surveyed concentrations of DA spiked in human serum (The inset show the good linearity between the absorbance ratio vs. DA concentration. (b) The recovery results of DA in human serum using the optimized sensing probes of Au@Agx5 NPs at pH 10 (Recovery of the method was calculated according to Kailasa methods [7]).

Reference

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