

Enzymeless biosensor based on β -NiS@rGO/Au nanocomposites for simultaneous detection of Ascorbic acid, Epinephrine and Uric acid

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1. Energy dispersive spectrum

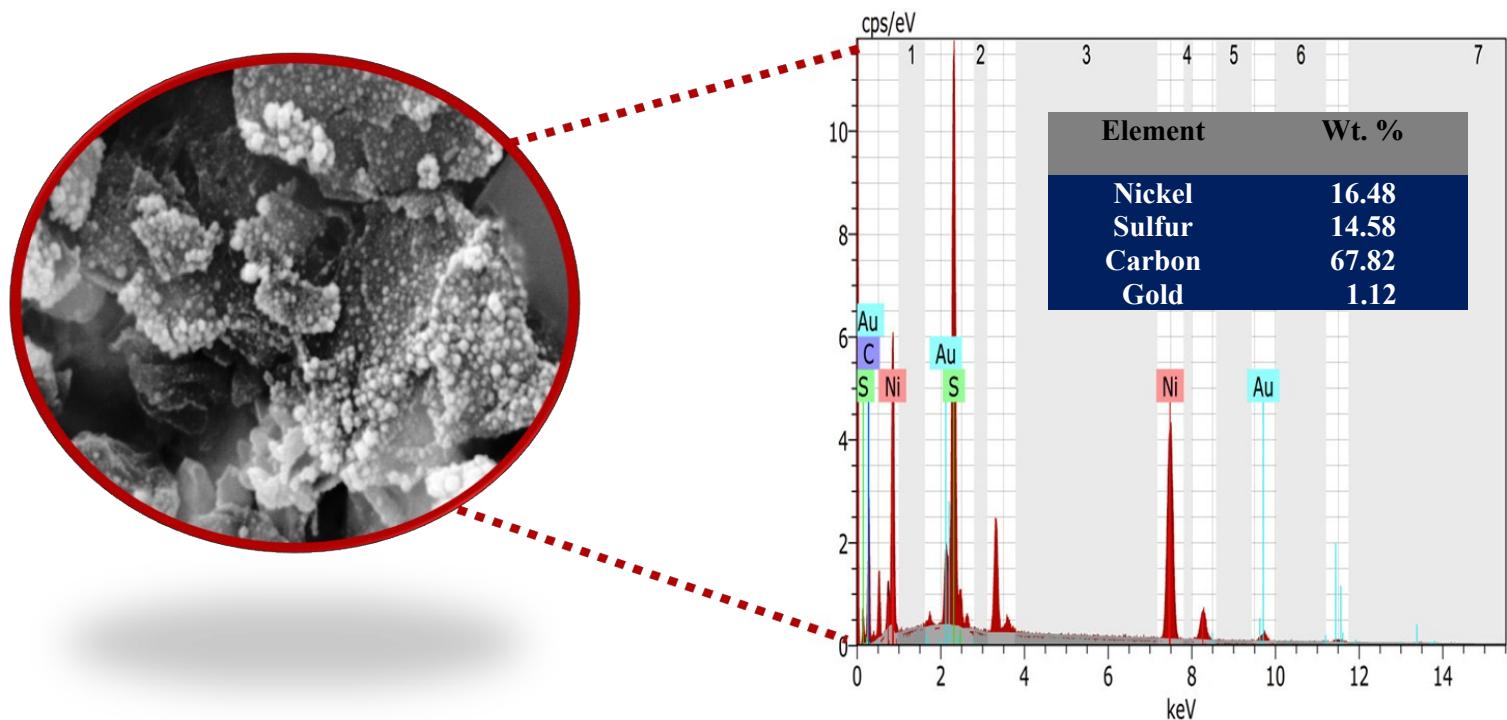


Fig. S1 EDX spectrum for β -NiS@rGO/AuNS hybrid composites with elemental atomic weight (%)

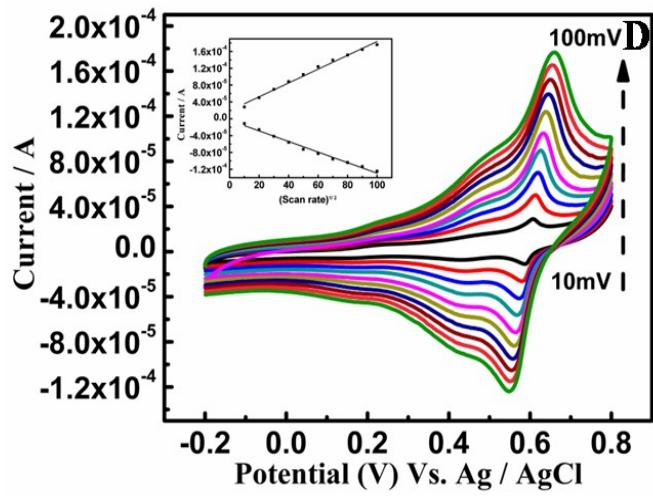
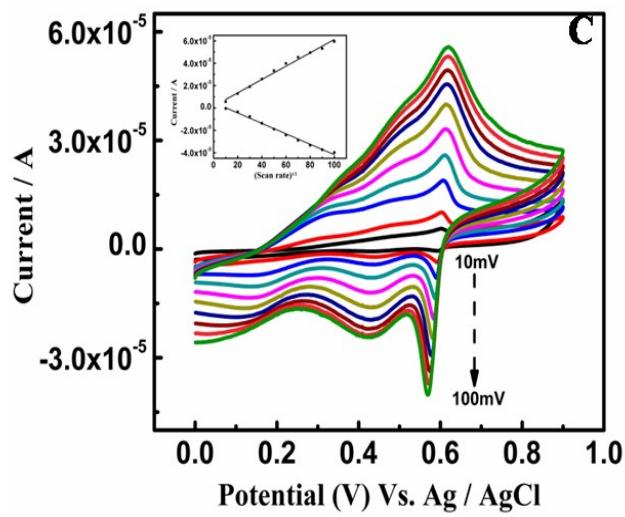
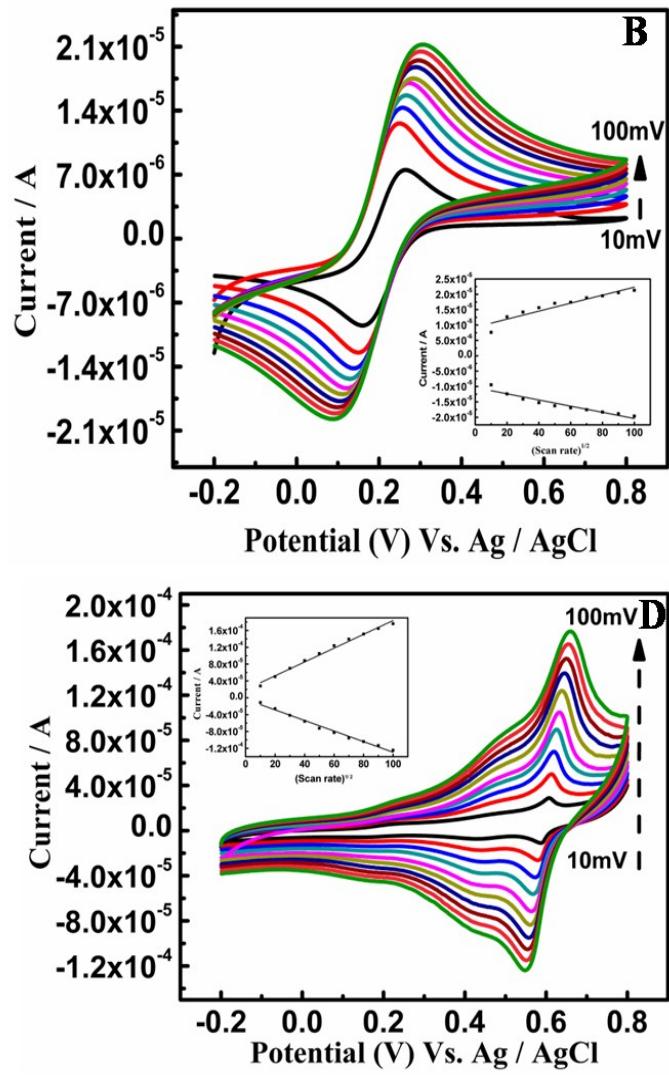
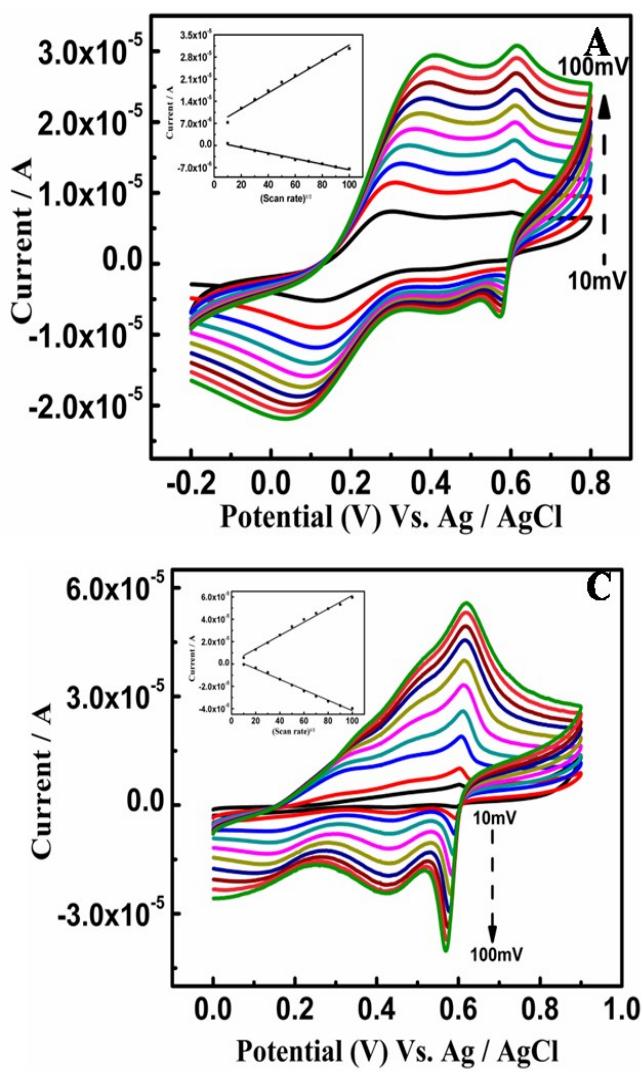


Fig. S2 CV behavior (A) β -NiS (B) GO (C) β -NiS@rGO (D) β -NiS@rGO/AuNS nano composites for different scan rate 10-100 mVs⁻¹ in presence of 1 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M KCl : Inset figure shows calibration curve of current versus square root of scan rate.

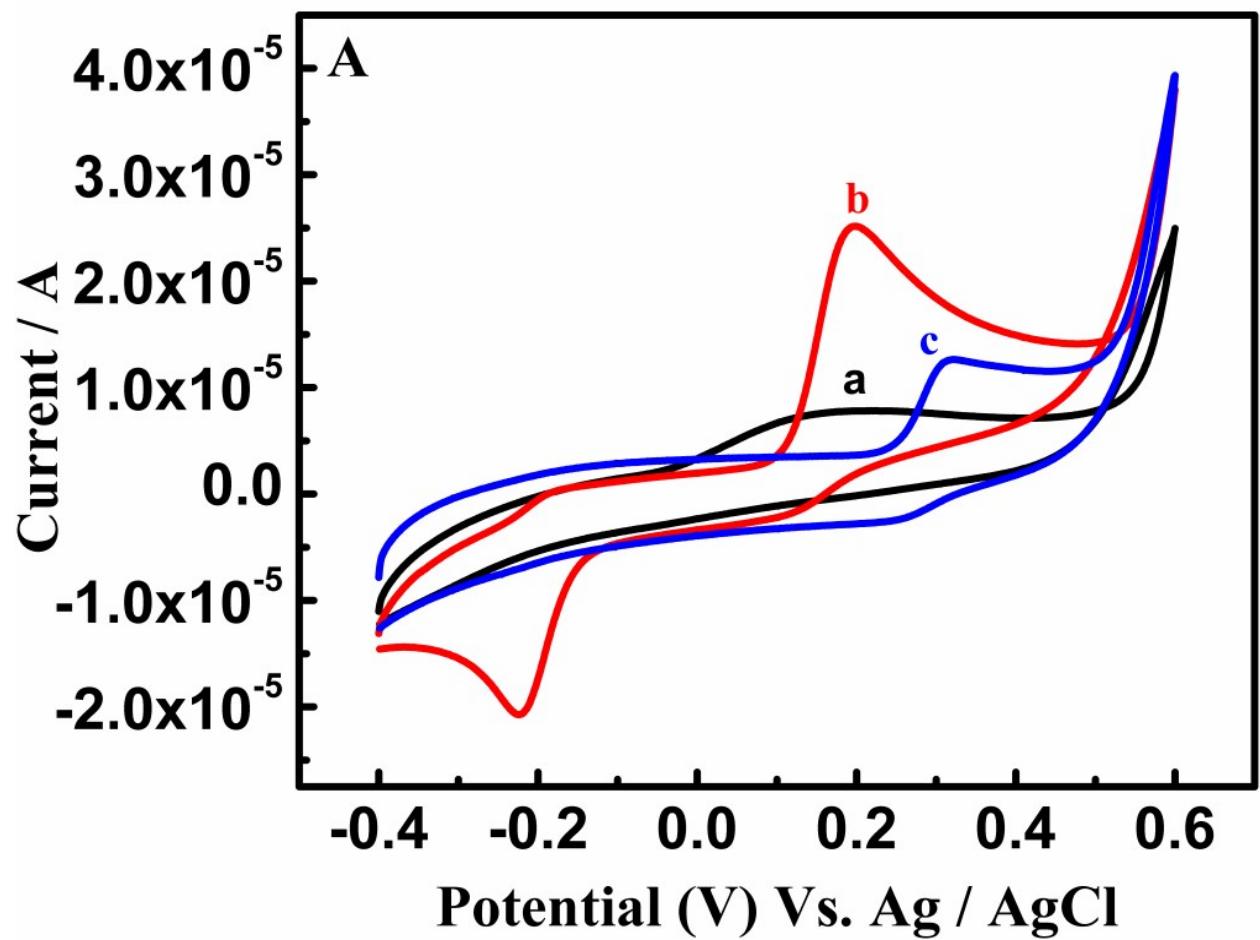


Fig. S3 500 μM of individual analyte of curve (a) AA (b) EP (c) UA in PBS (pH7.0) for the $\beta\text{-NiS@rGO/AuNS/GCE}$.

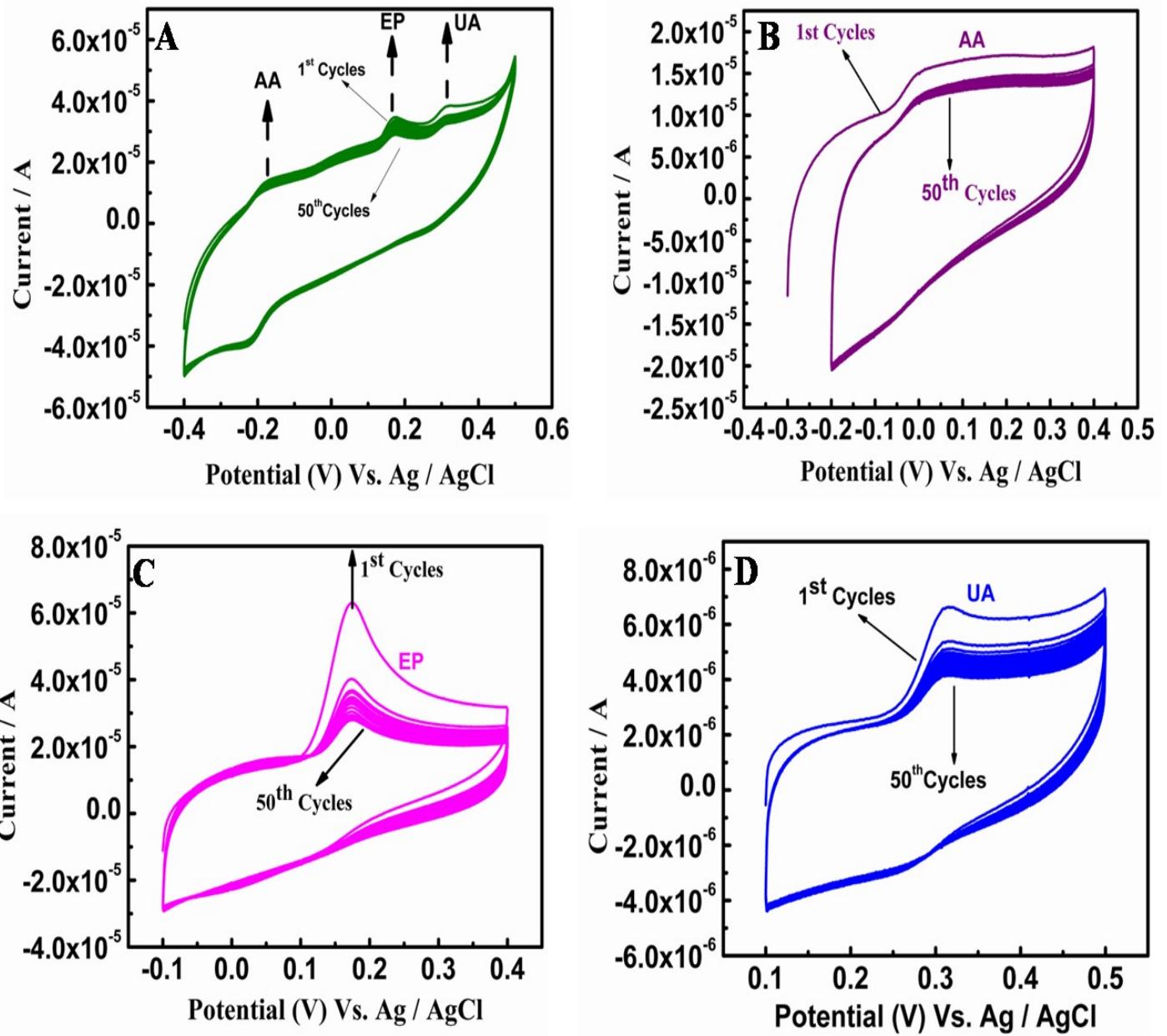


Fig. S4 stability studies (A) Simultaneous behavior of AA, EP and UA (B) Individual behavior of AA (C) EP (d) UA on $\beta\text{-NiS}@\text{rGO}/\text{AuNS}$ hybrid consecutive 50 cycles at scan rate 50mVs^{-1} presence of 1mM analyte in 0.1M PBS at (pH 7.0).

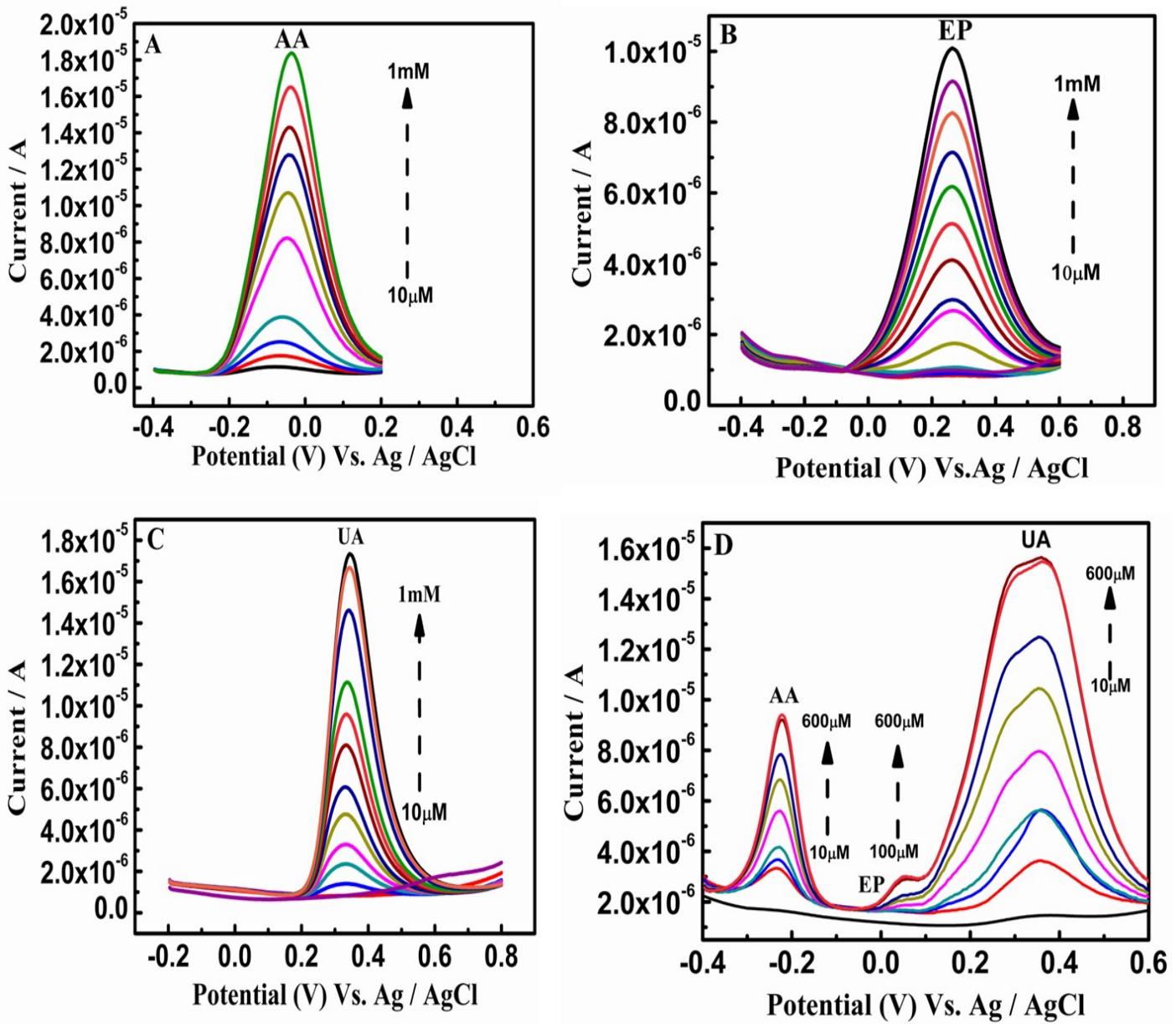


Fig. S5 SWV curves (A) Individual detection of AA $10\text{ }\mu\text{M}$ - 1 mM , (B) EP $10\text{ }\mu\text{M}$ - 1 mM and (C) UA $10\text{ }\mu\text{M}$ - 1 mM (D) Simultaneous detection of AA $10\text{ }\mu\text{M}$ - $600\text{ }\mu\text{M}$, EP $100\text{ }\mu\text{M}$ - $600\text{ }\mu\text{M}$ and UA $10\text{ }\mu\text{M}$ - $600\text{ }\mu\text{M}$ on modified β -NiS@rGO composite for each analyte in 0.1 M PBS (pH 7.0)

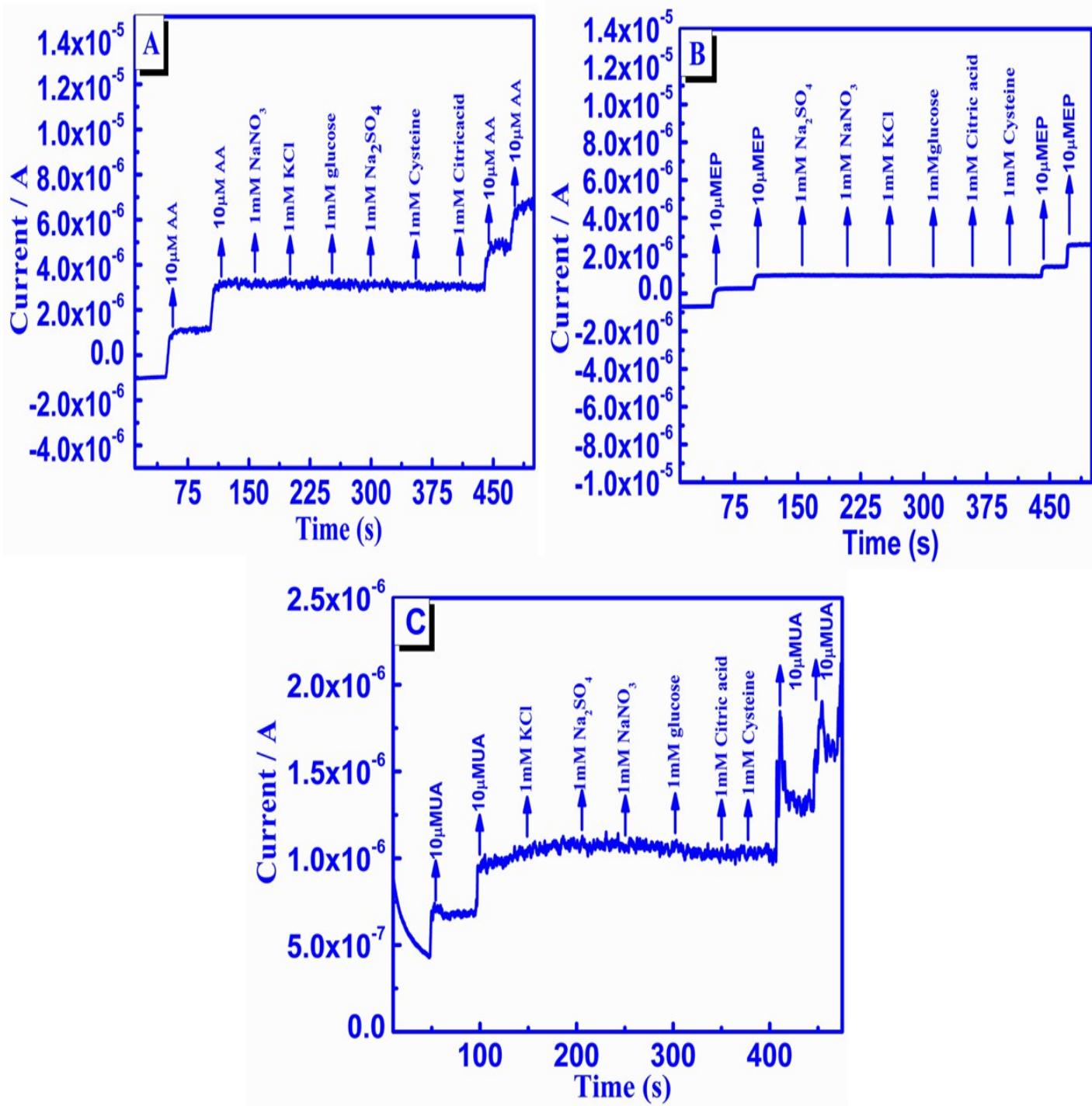
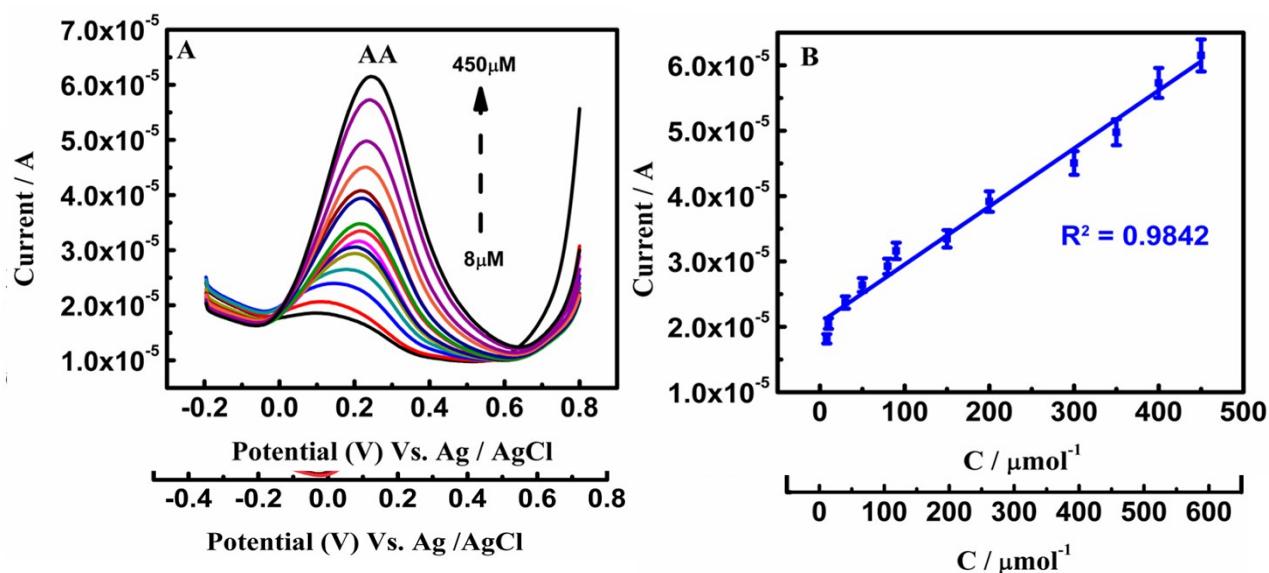


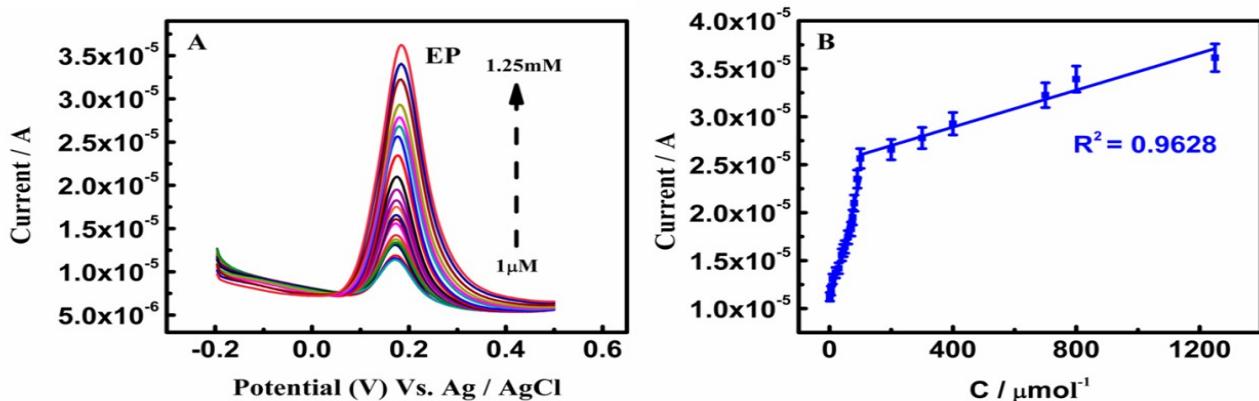
Fig. S6 Chronoamperometry responses of β -NiS@rGO/AuNS/GCE hybrid upon the successive addition of (a) 10 μ M AA (b) 10 μ M EP (c) 10 μ M UA and 1 mM of other interfering substances into stirring PBS (0.1 M, pH 7.0), The applied fixed potential at 0.119, 0.150, and 0.294V for AA, EP and UA respectively.

(1) Vitamin C with biotin tablet

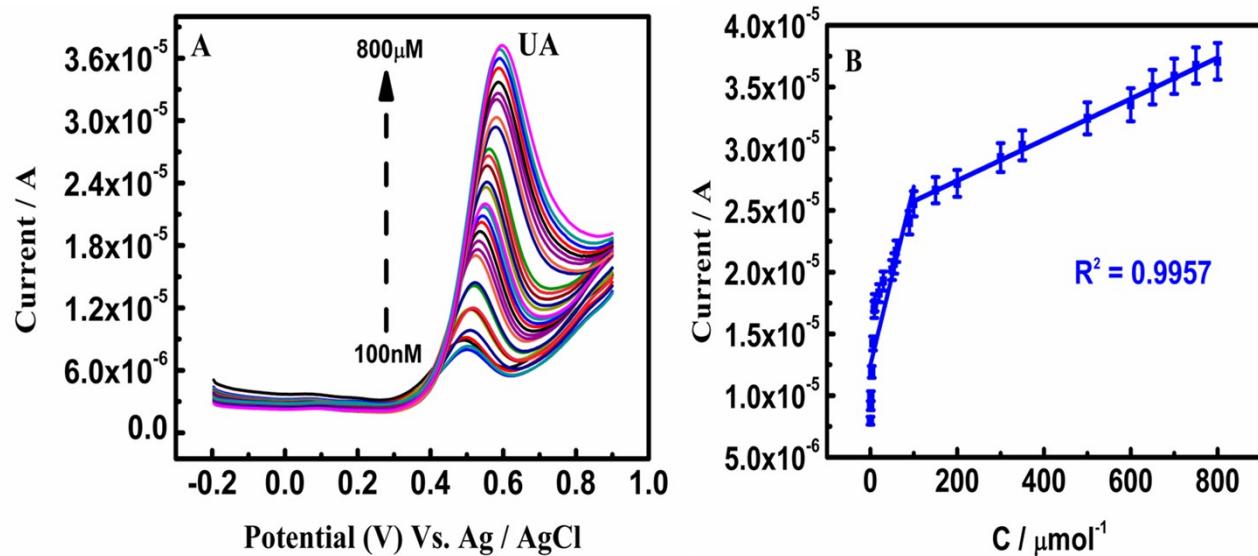


(2) Lemon fruit extract

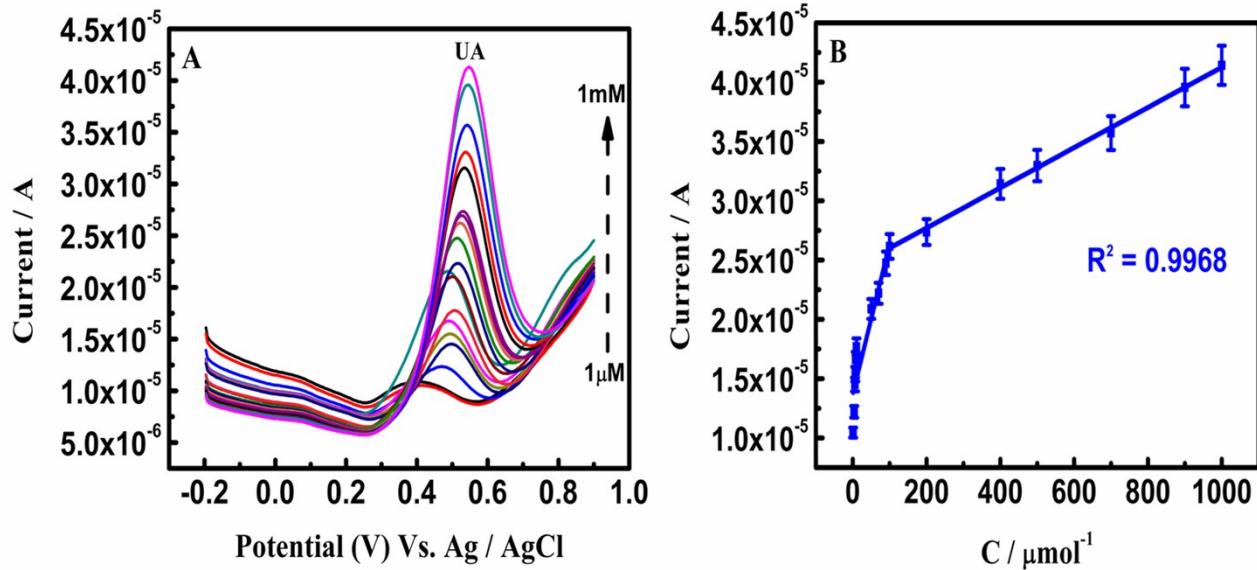
(3) Epinephrine hydrochloride injection



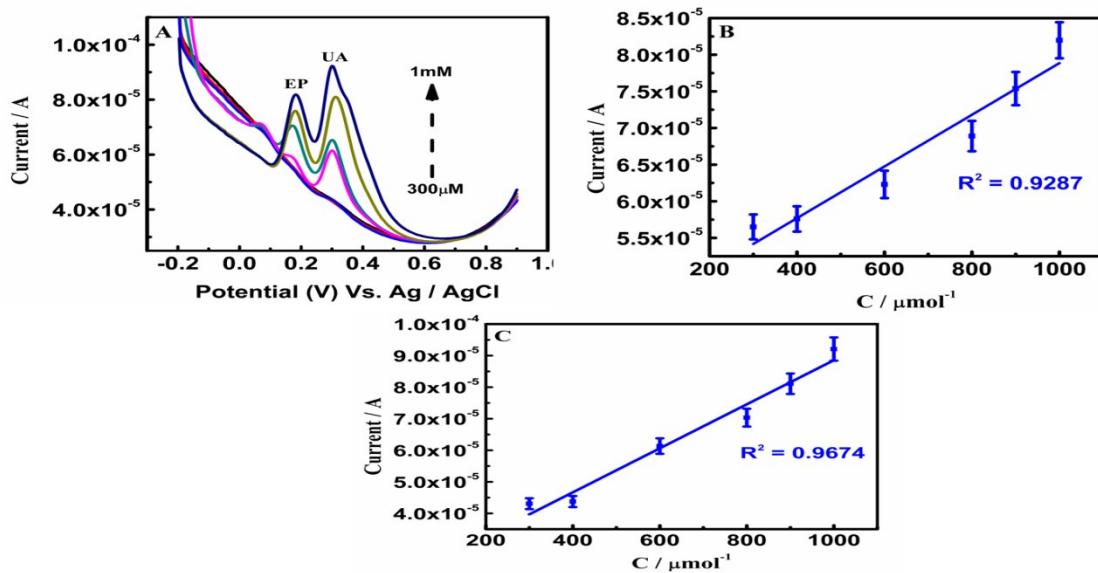
(4) Fresh human urine 1



(5) Fresh human urine 2



(6) Human serum



(7)

(8)

(9)

(10)

(7) Human blood

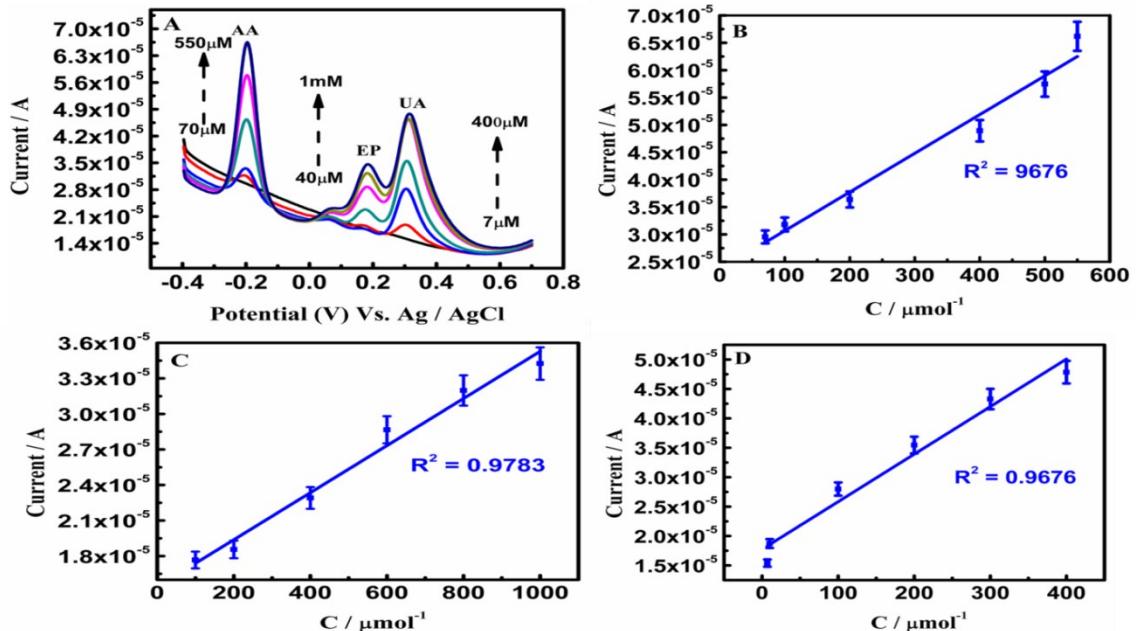


Fig. S7 SWV linear range response & calibration curve for practical utility of (1) Vitamin C with biotin tablet: AA (8-450 μ M), (2) Lemon extract: AA (8 μ M-600 μ M) (3) EP hydrochloride injection : EP (1 μ M-1.25 mM), (4) Fresh human urine 1: UA(100nM -800 μ M), (5) Fresh human urine 2 : UA(1 μ M-1 mM), (6) Human serum : EP, UA(300 μ M-1 mM), (7) Human blood : AA(70 μ M-550 μ M), EP(40 μ M- 1mM), UA(7 μ M-400 μ M).

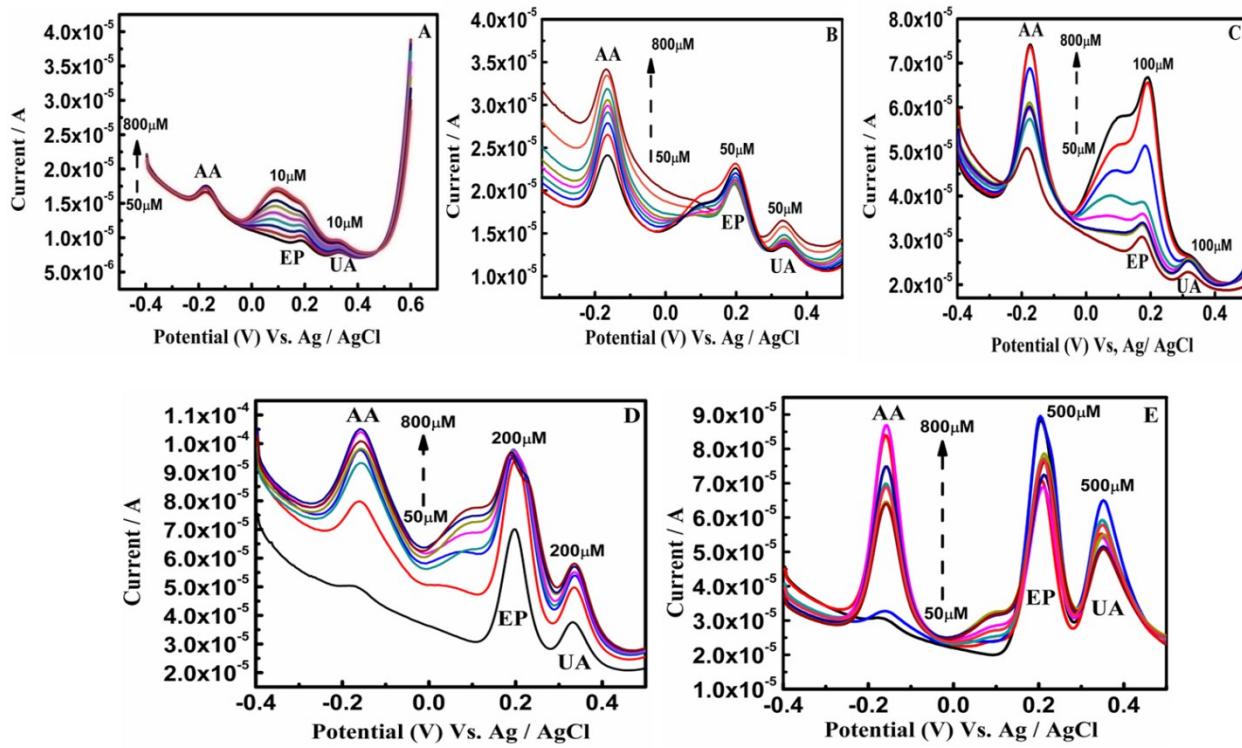


Fig. S8 SWV of constant concentration of EP, UA(10,50,100, 200 &500 μ M) and variable concentration of AA (50 μ M – 1mM)

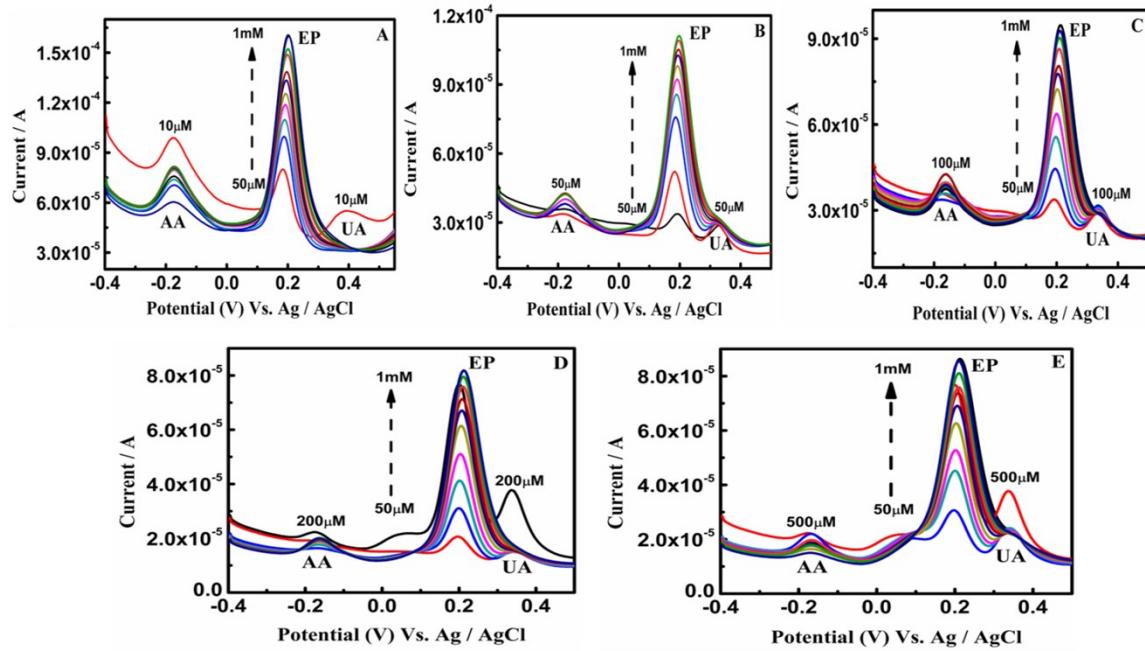


Fig.S9 SWV of constant concentration of AA, UA(10,50,100, 200 &500 μ M) and variable Concentration of EP (50 μ M – 1mM)

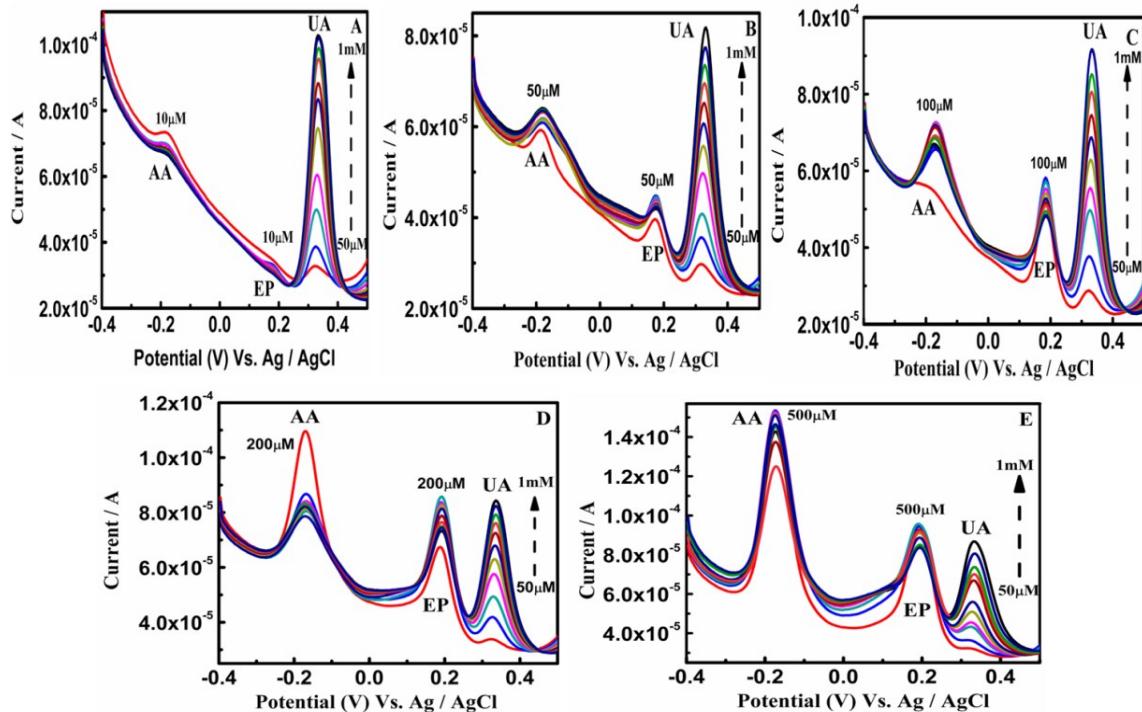


Fig.S10 SWV of constant concentration of AA, EP (10,50,100, 200 &500 μ M) and variable concentration of UA (50 μ M – 1mM)

S Table 1: Analytical performance of the different modified electrodes for the simultaneous determination of AA, EP and UA.

	Electrode material	Linear range(μ M)			Detection limit(μ M)			Ref
		AA	EP	UA	AA	EP	UA	
1	Caffeic acid / GCE	20 - 1000	2 - 80	5 - 300	7.0×10^{-6}	2.0×10^{-7}	6.0×10^{-7}	1
2	Poly (p-xylene sulfonephthalein) / GCE	10 - 1343	2 - 390	0.1 - 560	4	0.1	80	2
3	RuOHCF/MWCNT/GCE	0.2 - 15	0.1 - 10	0.90 - 250	0.08	0.05	0.59	3
4	Poly(Adizol Black B) / GCE	2 - 1.970	0.1 - 64	0.1 - 1.700	0.01	0.007	0.02	4
5	PMG/MWCNT/GCE	0.4 - 100	0.1 - 100	0.3 - 90	0.23	0.08	0.12	5
6	Poly(DA)-nanogold/GCE	40 - 1000	1.0 - 80	0.8 - 100	5.0	0.1	0.06	6
7	Au-NPs/poly(BCG)/GCE	5.0 - 1320	4.0 - 903	7.0 - 1500	0.2	0.01	0.004	7

8	poly(p-aminophenol)/GCE	6.0 - 70.0	0.4 - 8.0	0.4 - 8.0	1.0×10^{-6}	6.5×10^{-9}	1.8×10^{-7}	8
9	β -NiS@rGO-Au / GCE	1 μ M – 1mM	2 μ M – 1mM	100nM – 1mM	682nM	1.3 μ M	6nM	This work

S Table 2: Analytical performance of the different real biological sample for the simultaneous determination of AA, EP and UA on β -NiS@rGO/AuNS hybrid.

Voltammetric analysis of AA, EP, UA recovery test performed in Vitamin C tablet, Epinephrine hydrochloride injection, Human urine, blood, serum, lemon extract with β -NiS@rGO / Au , pH = 7.0						
Sample	Added (μ M) [AA, EP, UA]	Obtained (μ M) [AA, EP, UA]	Recovery (%) [AA, EP, UA]			
Vitamin C tablet	250, –, –	250, –, –	100, –, –			
Fresh human urine 1	–, –, 9	–, –, 9.05	–, –, 100.5			
Fresh human urine 2	–, –, 30	–, –, 31	–, –, 103.3			

–, 1000, 400	–, 975, 405	–, 97.5, 101.25
–, 500, –	–, 500, –	–, 100, –
200, –, –	190, –, –	95, –, –
7, 20, 6	7, 21.5, 6.6	100, 107.5, 110

References:

- 1 W .Ren, H .Qun Luo and N .Bing Li, *Biosens. and Bioelec.*, 2006, **21**, 1086-1092.
- 2 A. Ensafi, M .Taei and T .Khayamian, *Collo. and Surf. B: Biointer.*, 2001, **79**, 480-487.
- 3 J. B. Raoof, R .Ojani and M . Baghayeri, *Anal. Methods*, 2011, **3**, 2367-2373.
- 4 M .Taei and M .Jamshidi , *J. Soli. Stat. Electrochem.*, 2014, **18**, 673-683.
- 5 J .B.Raoof, R .Ojani and M .Baghayeri, *Turk. J. Chem.*, 2013, **37**, 36 -50.
- 6 Y. Zhang, W. Ren and S. Zhang, *Int. J. Electrochem. Sci.*, 2013, **8**, 6839-6850.
- 7 A .Ensafi B. Rezaei, S. Z. M. Zare and M .Taei, *Sens. and Actu. B*, 2010, **150**, 321-329.
- 8 C .C.Kocak and Z .Dursun, *J. Electroanal. Che.*, 2013, **694**, 94-103.