

## Supplementary Information

Cerium doped nickel-oxide nanostructures for riboflavin biosensing and antibacterial applications

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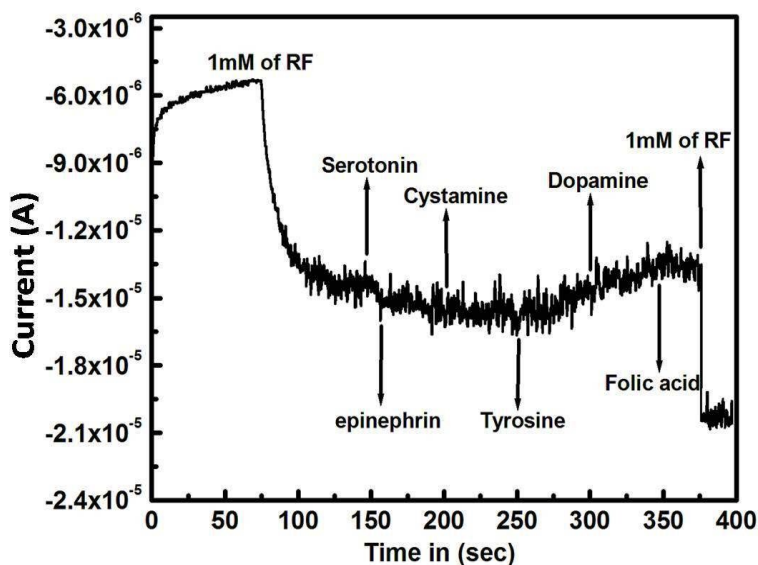
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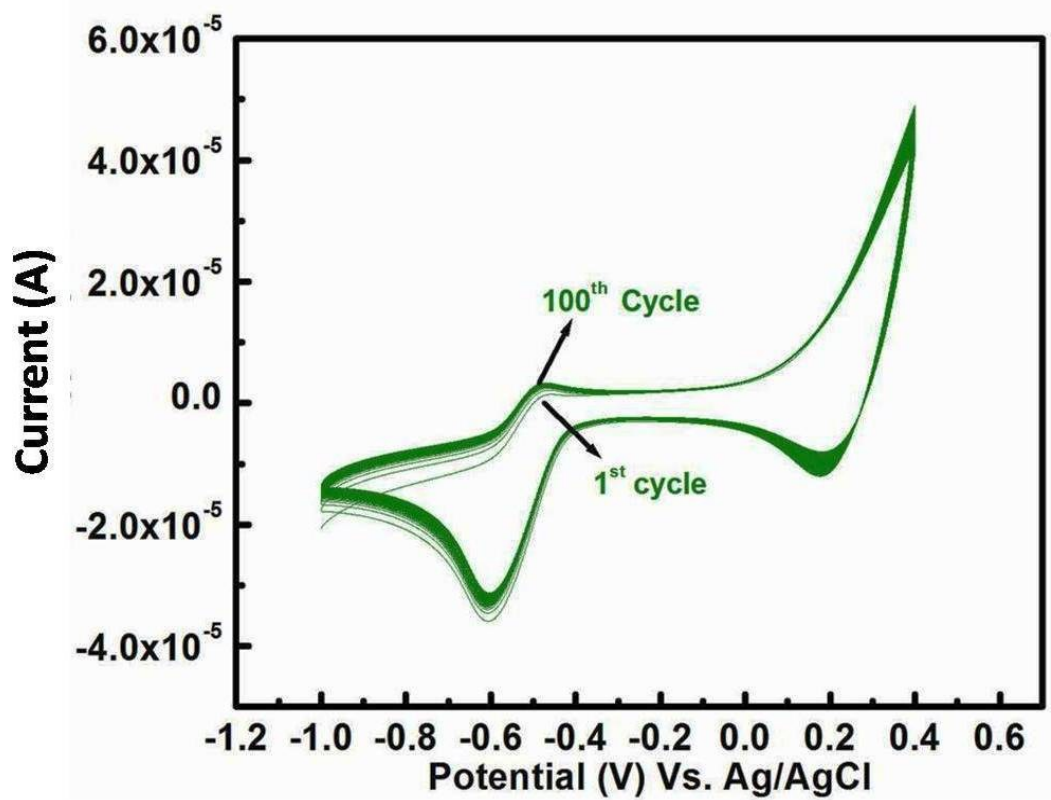
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**Figure S1.** Amperometric *i-t* curve for the addition of 1 mM of RF and 10 mM (10 fold) serotonin, epinephrine, cystamine, dopamine, tyrosine and final addition of 1 mM of RF at 5 wt.% Ce-NiO modified electrode in PBS (pH 7.2). Its applied potential -0.50 V.



**Figure S2.** 100 cycles of CVs of the modified GCE in presence of 1.0 mM RF 0.1 M KCl at a scan rate of  $100 \text{ mV s}^{-1}$

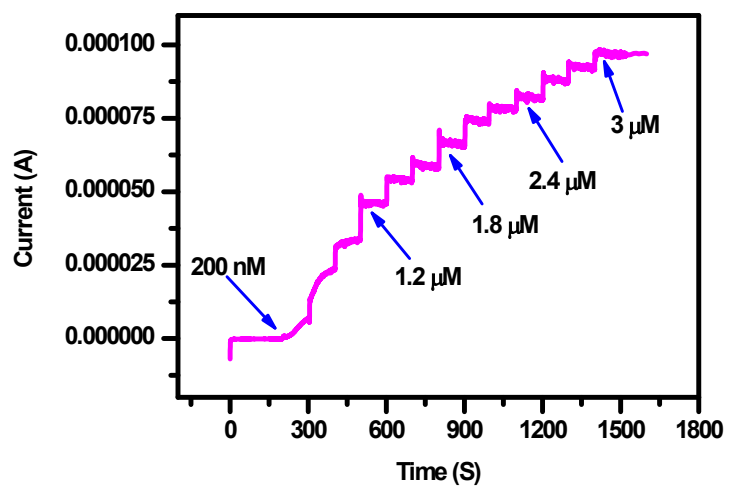


Figure S3. Amperometric responses at 5wt. % of Ce doped NiO modified GCE upon periodical addition of RF into 0.1M PBS at -0.5V

**Table S1** Crystallite Size for different percentage of Ce doping with NiO Samples

S.No	Sample	Size in nm
1	Pure NiO	90
2	1 wt.% of Ce doped NiO	85
3	3 wt.% of Ce doped NiO	74
4	5 wt.% of Ce doped NiO	72
5	7 wt.% of Ce doped NiO	57
6	9 wt.% of Ce doped NiO	41

**Table S2** Zone of inhibition (ZI), MIC and MBC values of sample a-f against various bacterial strains

Bacteria	Sample a			Sample b			Sample c			Sample d			Sample e			Sample f		
	ZI (mm)	MIC ( $\mu\text{g}/\text{mL}$ )	MBC ( $\mu\text{g}/\text{mL}$ )	ZI (mm)	MIC ( $\mu\text{g}/\text{mL}$ )	MBC ( $\mu\text{g}/\text{mL}$ )	ZI (mm)	MIC ( $\mu\text{g}/\text{mL}$ )	MBC ( $\mu\text{g}/\text{mL}$ )	ZI (mm)	MIC ( $\mu\text{g}/\text{mL}$ )	MBC ( $\mu\text{g}/\text{mL}$ )	ZI (mm)	MIC ( $\mu\text{g}/\text{mL}$ )	MBC ( $\mu\text{g}/\text{mL}$ )	ZI (mm)	MIC ( $\mu\text{g}/\text{mL}$ )	MBC ( $\mu\text{g}/\text{mL}$ )
<i>K. pneumoniae</i>	-	>100	>100	-	>100	>100	9	70	80	11	30	40	10	30	40	-	>100	>100
<i>S. typhi</i>	13	30	30	9	80	90	15	30	40	17	20	30	15	20	30	12	40	50
<i>P. aeruginosa</i>	12	50	60	10	60	70	11	40	50	14	30	40	11	50	60	10	60	70
<i>B. cereus</i>	12	50	60	10	60	60	12	50	50	14	30	40	11	30	40	10	40	40
<i>B. subtilis</i>	17	20	30	15	20	20	20	10	20	22	10	10	17	10	20	15	20	30
<i>S. aureus</i>	17	20	20	14	20	30	15	20	20	18	10	20	16	20	30	13	30	30

\* The values are mean of triplicate experiments

**Table S3** Comparison of the efficiency of reported electrochemical methods in the determination of RF

Electrode	limit of detection	linear range	reference
(1) P3MT/GCE	$5.0 \times 10^{-8} \text{ mol L}^{-1}$	$1.0 \times 10^{-7} - 2.0 \times 10^{-4} \text{ mol L}^{-1}$	[1]
(2) Aza / PCPE	$0.2 \text{ ng cm}^{-1}$	$0.5 \text{ ng cm}^{-3}$ to $70 \mu\text{g cm}^{-3}$	[2]
(3) DNA/CNT	$0.2 \text{ ng L}^{-1}$	$5.31 \times 10^{-13} \text{ mol L}^{-1}$ -	[3]
(4) C -18/AuE	$2.3 \mu\text{g mL}^{-1}$	-	[4]
(5) CILE	$0.1 \text{ nM}$	$0.8 - 110 \text{ nM}$	[5]
(6) Ag amalgam film	$0.009$	$0.05 - 3$	[6]
(7) AgSAEs	$8.2 \times 10^{-10} \text{ mol L}^{-1}$ (m - AgSAE) and $1.3 \times 10^{-9} \text{ mol L}^{-1}$ (p-AgSAE)	-	[7]
(8) $\text{WO}_3 - \text{TiO}_2 / \text{ITO}$	$1.87 \times 10^{-7} \text{ M}$	$3.23 \times 10^{-7}$ to $4.0 \times 10^{-5} \text{ M}$	[8]
(9) Ds-DNA/ PCE	$0.34 \mu\text{g mL}^{-1}$	$0.5 - 70 \mu\text{g mL}^{-1}$	[9]
(10) Cr- $\text{SnO}_2 / \text{GCE}$	$107 \text{ nM}$	$0.2 \times 10^{-6}$ to $1.0 \times 10^{-4} \text{ M}$	[10]
(11) $\alpha - \text{Fe}_2\text{O}_3/\text{MWCNT}/\text{AuNP}$	$6 \text{ nM}$	$50 \times 10^{-9}$ to $600 \times 10^{-6}$	[11]

## References:

- (1) Zhang, H.; Zhao, J.; Liu, H.; Wang, H.; Liu, R.; Liu, J.; Application of Poly (3-methylthiophene) Modified Glassy Carbon Electrode as Riboflavin Sensor. *Int. J. Electrochem. Sci.* **2010**, *5*, 295
- (2) Kotkar, M.; Desai P,B.; Srivastava, A,K. Behavior of riboflavin on plain carbon paste and aza macrocycles based chemically modified electrodes, *Sensor Actua. B* **2007**,124, 90.
- (3) Ly,Y.; Yoo, H.S.; Ahn, J.Y.; Nam, K.H. Pico molar assay of riboflavin in human urine using voltammetry, *Food Chem.* **2011**, 127, 270.
- (4) Balco, E.; Dominguez, C.S.H.; Hernandez, Alkanethiols, J.V. Modified Gold Electrodes for Selective Detection of Molecules with Different Polarity and Molecular Size. Application to Vitamin B2 Analysis *Electroanalysis* **2009**, 21, 495.
- (5) Safavi, A.; Maleki, N.; Ershadifar, H.; Tajabadi, F. Development of a sensitive and selective Riboflavin sensor based on carbon ionic liquid electrode, *Anal. Chim. Acta* **2010**, 674, 176.
- (6) Bas .S.Lakubowska, S.; Girski, M. Application of renewable silver amalgam annular band electrode to voltammetric determination of vitamins C, B<sub>1</sub> and B<sub>2</sub>, *Talanta* **2011**, 84,1032.
- (7) Bandzuchova, L.; Selesovska, R.; T.Navratil, T.; Chylkov, J. Voltammetric monitoring of electrochemical reduction of riboflavin using silver solid amalgam electrodes, *Electrochim. Acta* **2012** ,75,316
- (8) Li, Y.; Hsu, P. C.; S.M. Chen. Multi-functionalized biosensor at WO<sub>3</sub>-TiO<sub>2</sub> modified electrode for photoelectrocatalysis of norepinephrine and riboflavin, *Sensor Actuat. B* **2012**, 174, 427.
- (9) Ensafi, Heydari-Bafrooei, E.; Amini, M. DNA-functionalized biosensor for riboflavin based electrochemical interaction on pretreated pencil graphite electrode, *Biosens. Bioelectron.* **2012**,31,376.

- (10) Lavanya, N.; Radhakrishnan, S.; Sekar, C.; Navaneethan, M. Fabrication of Cr doped SnO<sub>2</sub> nanoparticles based biosensor for the selective determination of riboflavin in pharmaceuticals, *Analyst* **2013**, 138, 2061.
- (11) Sumathi, C.; Muthukumar, P.; Radhakrishnan, S.; Ravi, G.; Wilson, J. Riboflavin detection by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/MWCNT/AuNPs-based composite and a study of the interaction of riboflavin with DNA. *RSC Adv.* **2015**, 5, 17888-17896

**Table S4** Determination of the riboflavin content in commercial pharmaceutical products and milk powder by SWV on the 5 wt. % of Ce-doped NiO modified electrode.

Sample	Reported content (mg)	Content found (mg)	Recovery %
multivitamin tablet	1.6	1.45	90.6
multivitamin capsule	2	1.8	90
Milk powder	0.78	0.70	89.7