Anal. Bioanal. Electrochem., Vol. 15, No. 9, 2023, 726-738 (Supplements)
https://www.doi.org/10.22034/abec.2023.708104

Analytical&
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Electrochemistry

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Supplementary Materials

Electrochemical Measurement of Β-Nicotinamide Adenine Dinucleotide by ZrO_2 Modified Carbon Paste Electrode

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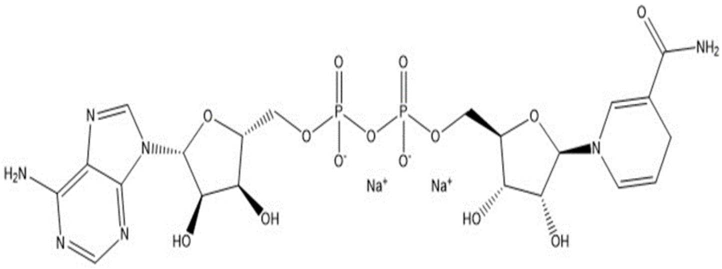

Scheme 1. NADH structure

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1. Modifier optimization

Cyclic voltammograms were recorded for DBC/CPE electrode in 0.1M phosphate buffer with pH = 7.0 at a scan rate of 20 mV s^{-1} for different amounts of DBC modifier, without the presence of NADH (Figure S1) and in the presence of 0.2 mM of NADH (Figure S2). These voltammograms show the effect of the amount of DBC modifier on the electrocatalytic current response of the electrode. As can be seen, with the increase in the amount of the modifier, due to the fact that more electrons participate in the reaction, the amount of current also increases. On the other hand, by increasing the amount of the modifier, due to the kinetic limitation, the current does not increase. So the optimum value of the modifier is considered to be 1%, which shows the maximum amount of current according to the results. Also, according to Figure S2, we can conclude that in the presence of NADH, the electrocatalytic current response rate increases, which confirms the EC' mechanism.

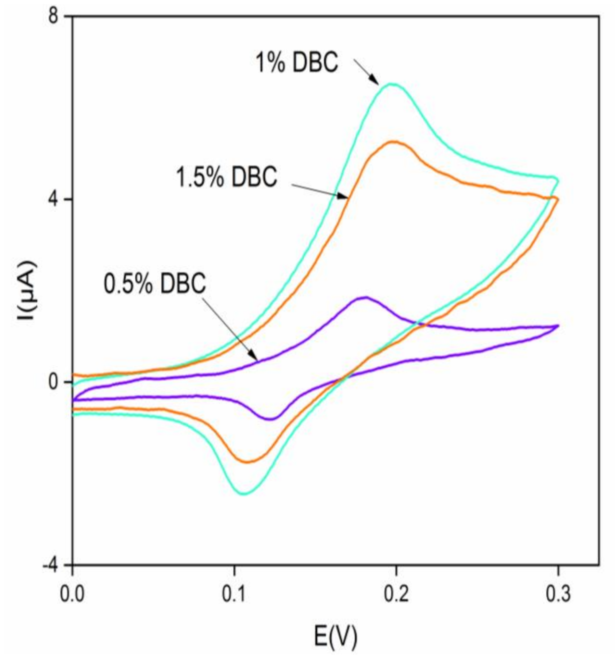

Figure S1. Cyclic voltammogram of DBC/CPE electrode containing 0.5 wt%, 1 wt% and 1.5 wt% of DBC modifier in 0.1 M phosphate buffer solution with pH = 7.0 at scan rate of 20 mV s^{-1} in the potential range 0.0-0.3 V

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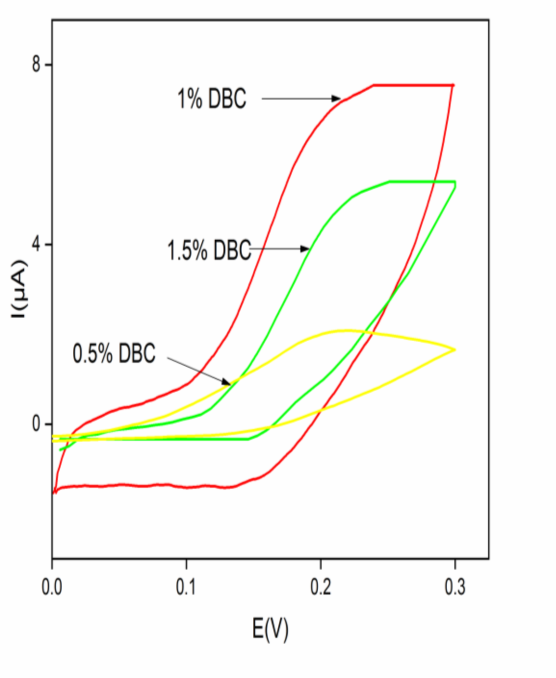

Figure S2. Cyclic voltammogram of DBC/CPE electrode containing 0.5 wt%, 1 wt% and 1.5 wt% of DBC modifier in 0.1 M phosphate buffer solution with pH = 7.0 and NADH 0.2 mM at scan rate of 20 mV s^{-1} in the potential range 0.0-0.3 V

2. ZrO_2 nanoparticle optimization

Cyclic voltammograms were recorded for DBC/ZrO_2/CPE electrode with various amounts of ZrO_2 nanoparticles and optimum amount of DBC modifier (1%) in 0.1M phosphate buffer with pH=7.0 at scan rate of 20 mV s^{-1} without the presence of NADH (Figure S3) and in the presence of 0.2 mM of NADH (Figure S4). The current response of these voltammograms shows the effect of the amount of ZrO_2 nanoparticles on the electrocatalytic current response of the electrode. According to Figure S3, 3% ZrO_2 nanoparticle shows a higher current response. Also, Figure S4 compares the effect of the presence or absence of NADH on the amount of electrocatalytic current, which shows the increase in the electrocatalytic current response in the presence of 0.2 mM NADH as a result of EC' mechanism.

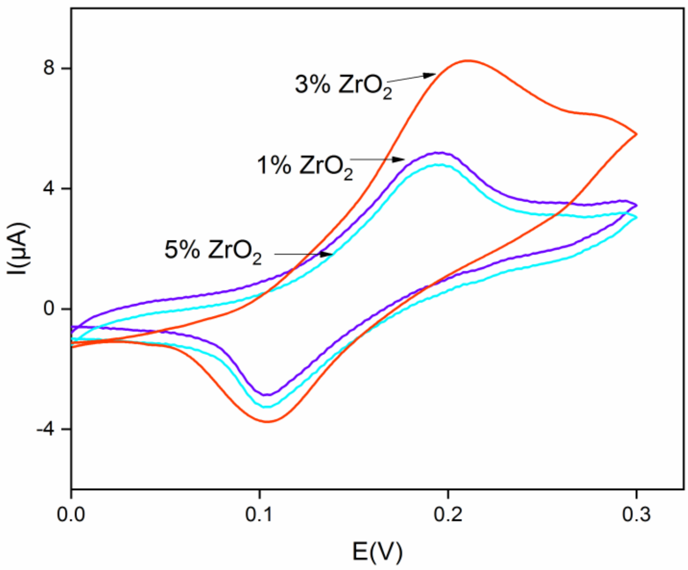

Figure S3. Cyclic voltammogram of DBC/ZrO_2/CPE electrode containing 0.5 wt%, 1 wt% and 3 wt% of ZrO_2 nanoparticle in 0.1 M phosphate buffer solution with pH = 7.0 at scan rate of 20 mV s^{-1} in the potential range 0.0-0.3 V

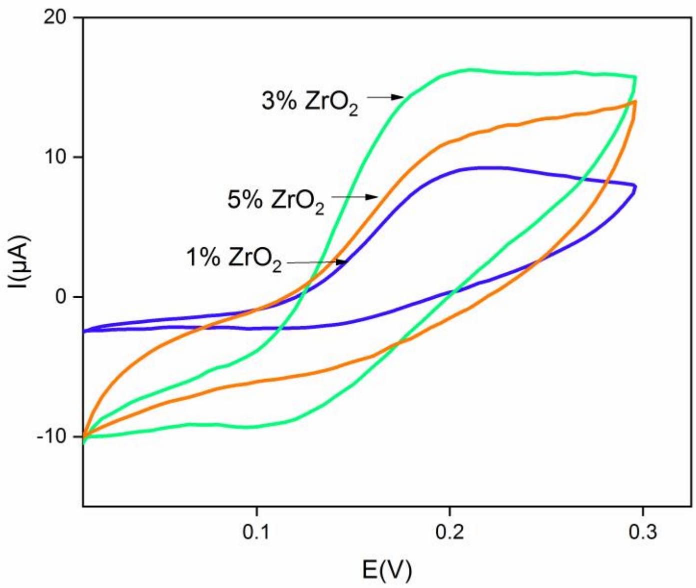

Figure S4. Cyclic voltammogram of DBC/ZrO_2/CPE electrode containing 0.5 wt%, 1 wt% and 3 wt% of ZrO_2 nanoparticle in 0.1 M phosphate buffer solution with pH =7.0 and NADH 0.2 mM at scan rate of 20 mV s^{-1} in the potential range 0.0-0.3 V

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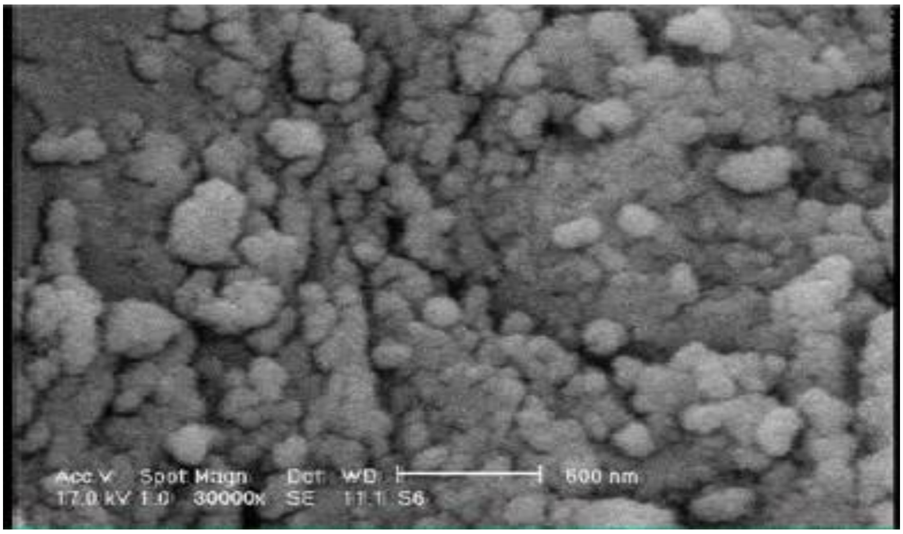

Figure S5. SEM image of ZrO_2 nanoparticles

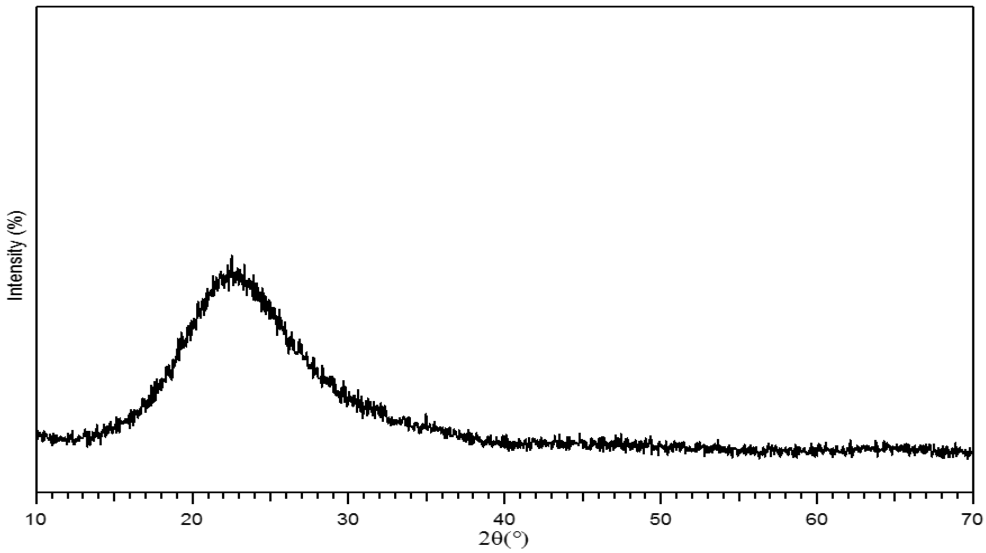

Figure S6. XRD spectrum of ZrO_2 nanoparticles

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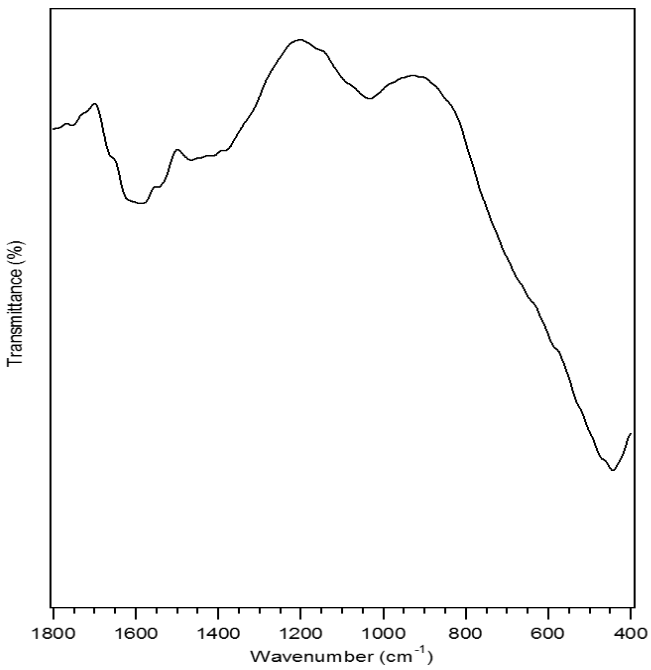


Figure S7. FT-IR spectrum of ZrO_2 nanoparticles

3. Structure and characterizations of DBC Modifier

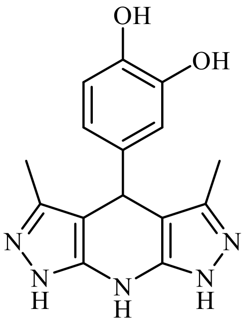


Figure S8. Structure of DBC modifier

Characterizations:

Redish brown solid, m.p. 208-210 °C**.**

FT-IR (ATR) ῡ (cm^{-1}): 3496, 3220, 1597, 1527, 1469, 1249, 1112, 829, 782, 726.

^{1}H NMR (400 MHz, DMSO-d$_6$) /δ ppm: 11.30 (s, NH, 3H), 8.63 (s, OH, 1H), 8.52 (s, OH, 1H), 6.56 (d, *J*=8 Hz, 1H), 6.55 (s, 1H), 6.35 (d, *J*=8 Hz, 1H), 4.67 (s, 1H), 2.06 (s, 6H).

^{13}C NMR (100 MHz, DMSO-d$_6$) /δ ppm: 161.5, 144.9, 143.4, 140.2, 134.5, 118.5, 115.6, 115.3, 105.1, 32.3, 10.8.

Anal. Calcd for $C_{15}H_{15}N_5O_2$ (297.31): C, 60.60; H, 5.09; N, 23.56. Found: C, 60.75; H, 5.15; N, 23.45.

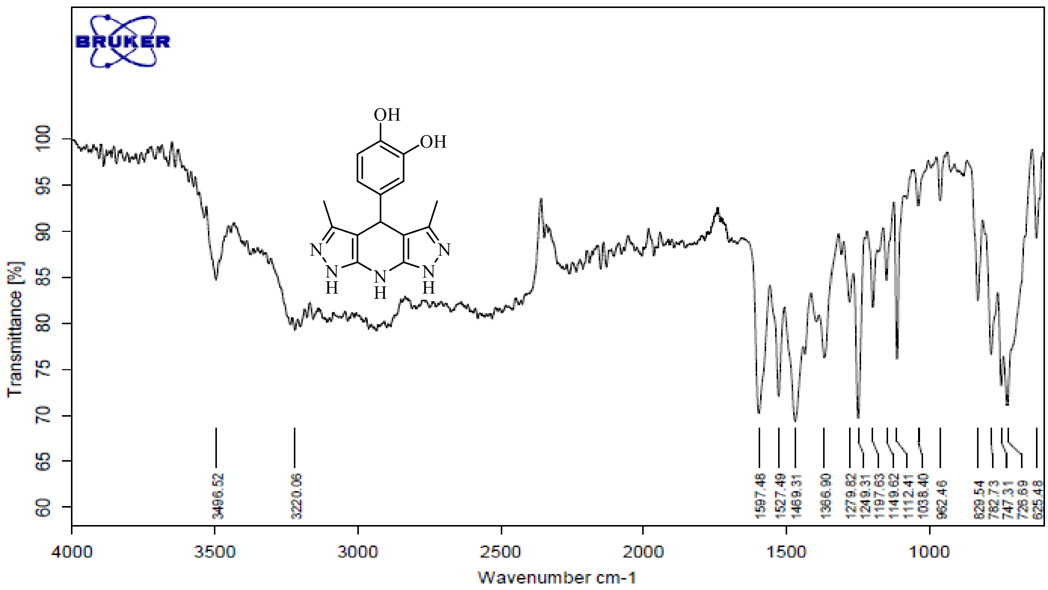
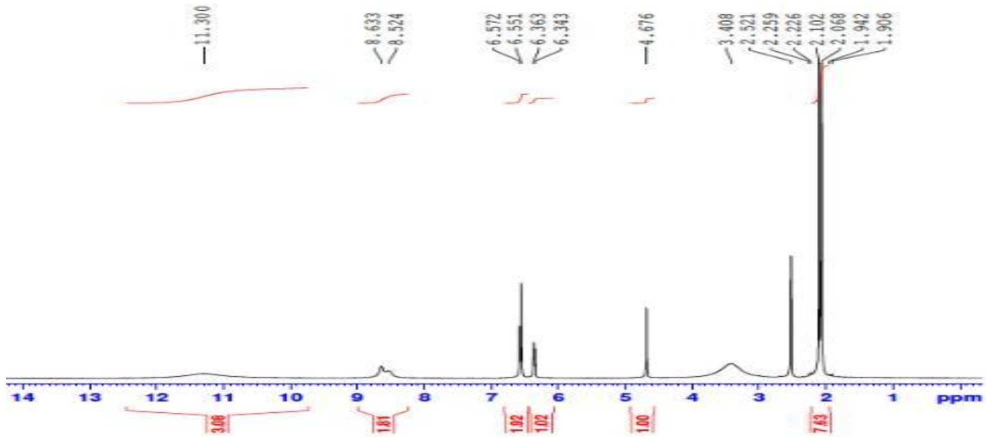


Figure S9. FT-IR spectrum of DBC modifier



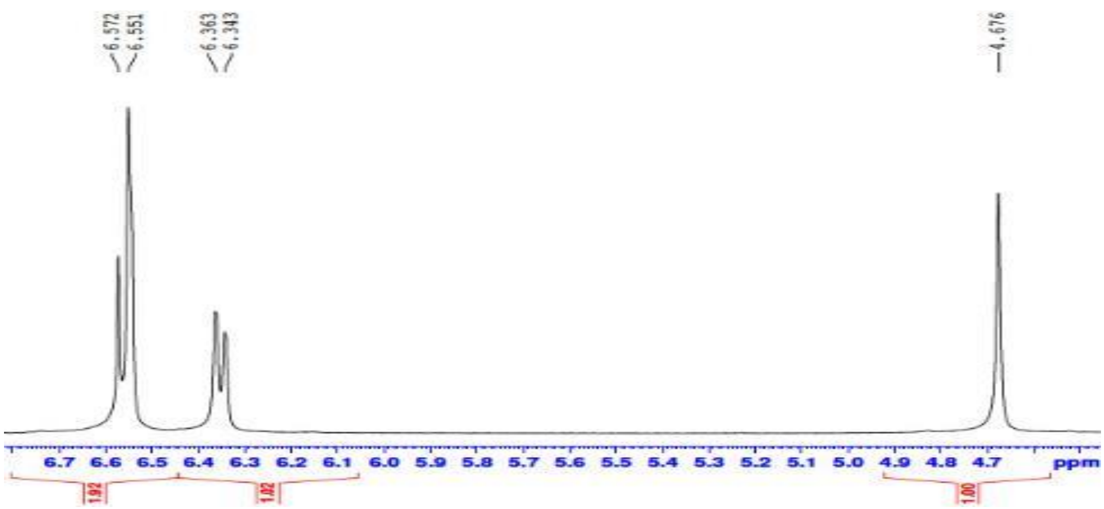


Figure S10. ^{1}H NMR (400 MHz, DMSO-d_6) for DBC modifier

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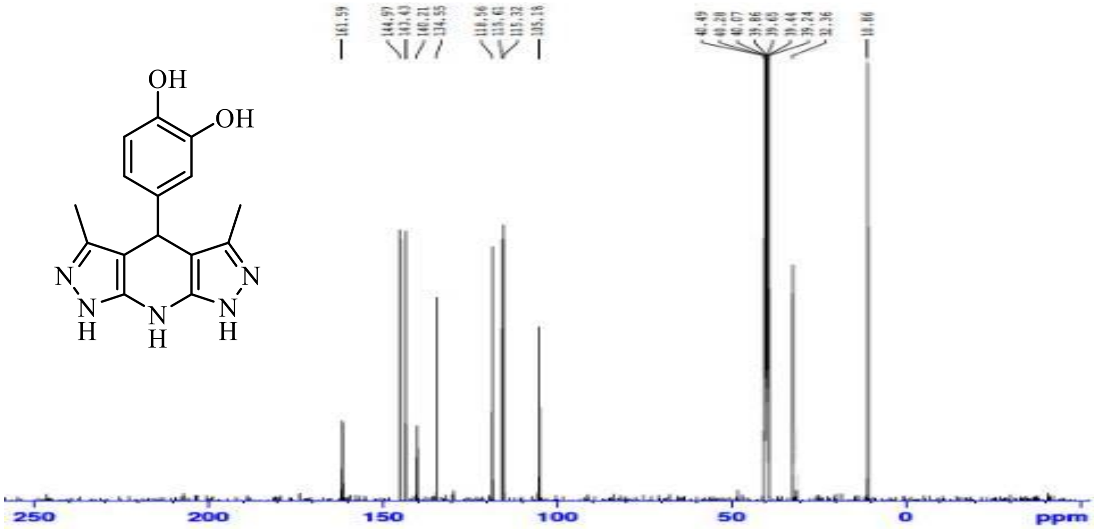

Figure S11. ^{13}C NMR (100 MHz, DMS-d$_6$)

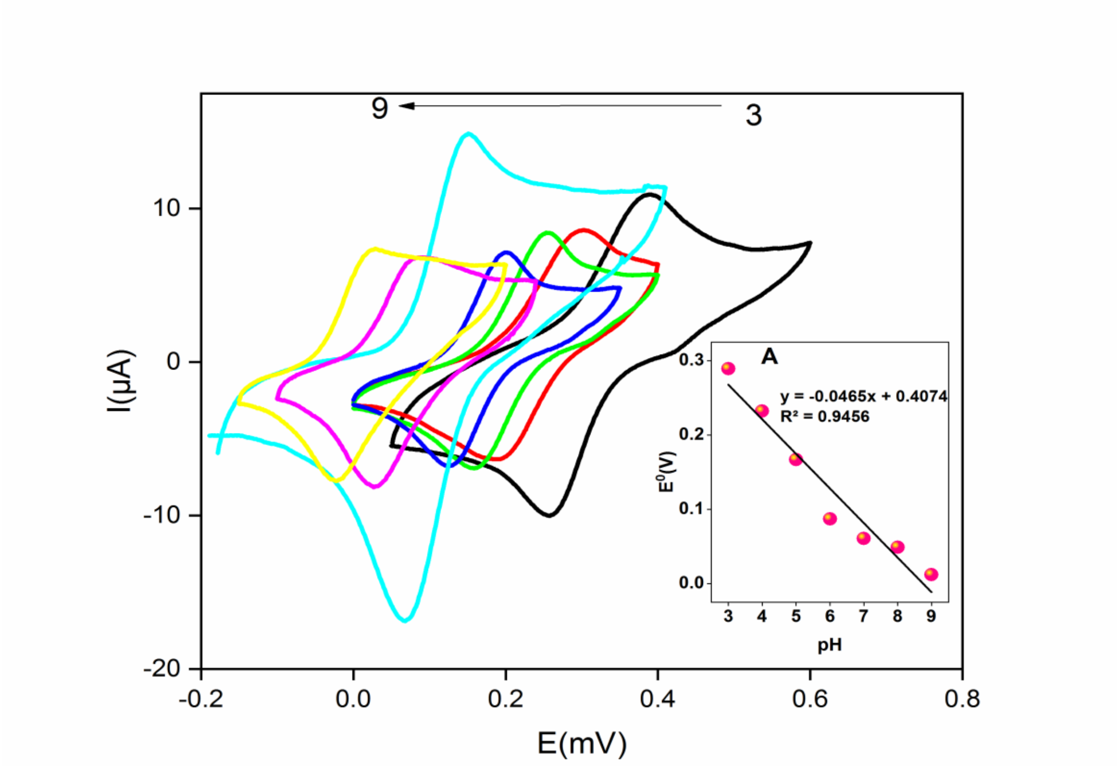

Figure S12. Cyclic voltammograms of DBC/ZrO_2 /CPE electrode in 0.1M phosphate buffer solution with different pHs from 3.0-9.0 at a scan rate of 100 mV s^{-1}. (A) The plot of $E^{0'}$ s pH

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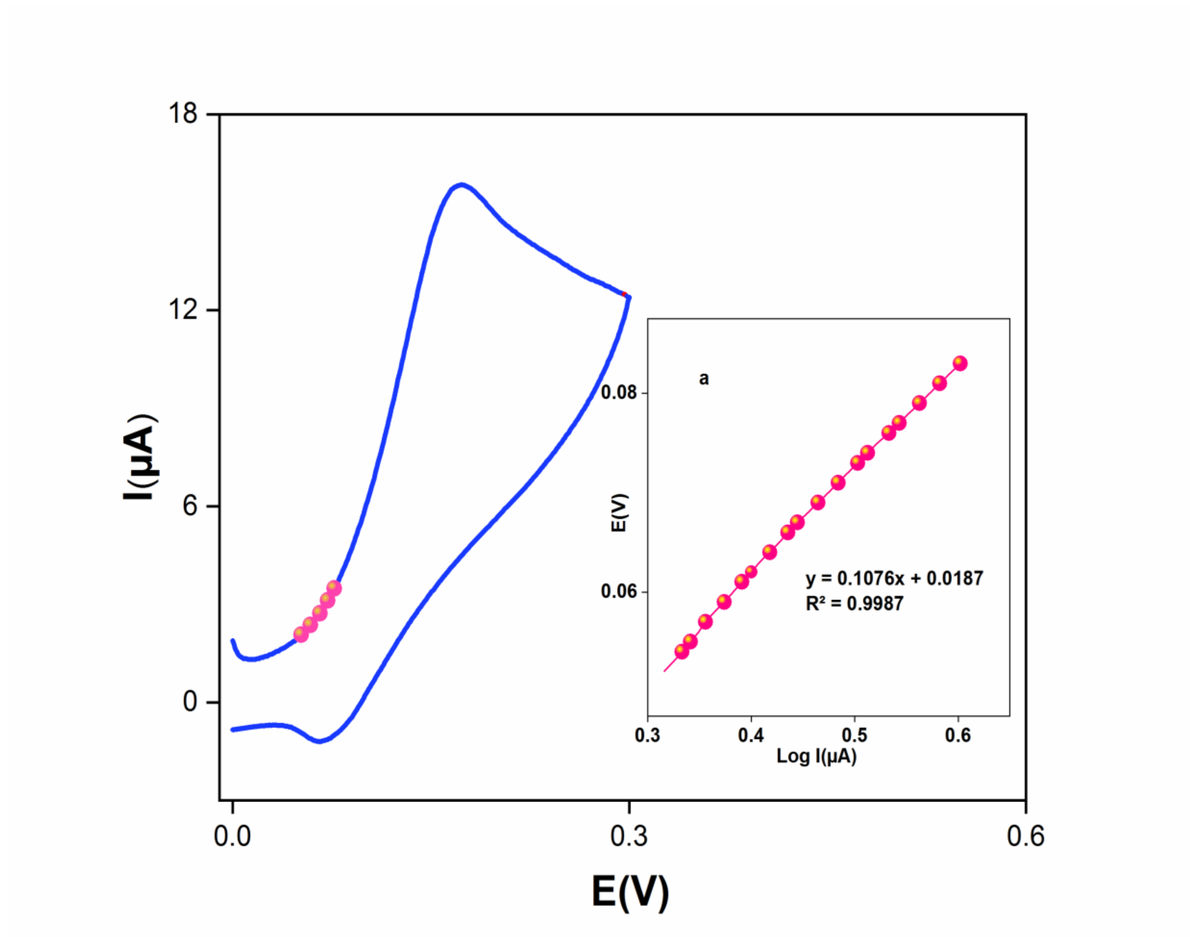

Figure S13. Cyclic voltammogram of DBC/ZrO_2/CPE in 0.1 M phosphate buffer with pH=7.0 with the presence of 0.4 mM of NADH at a scan rate of 20 mV s^{-1}. Inside (a) showing Tofel plot (potential versus logarithm of current intensity).

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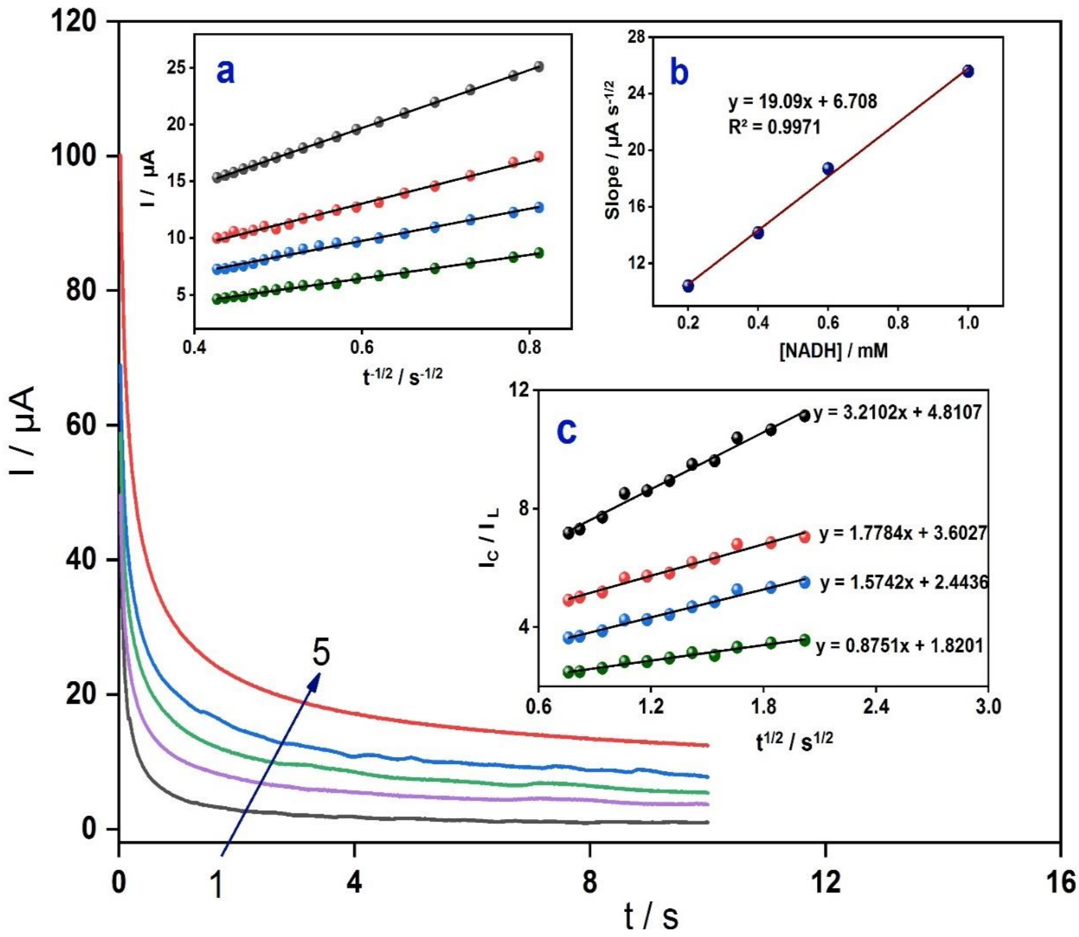

Figure S14. Chronoamperograms of DBC/ZrO_2/CPE electrode in phosphate buffer 0.1M with pH=7.0 for different concentrations of NADH. Inset (a) NADH electrocatalytic current curve versus the inverse of the square root of time ($t^{-1/2}$) obtained from chronoamprograms of 0.2, 0.4, 0.6 and 1.0 mM of NADH, (b) showing the plot of the obtained slopes of graph A for different concentrations of NADH

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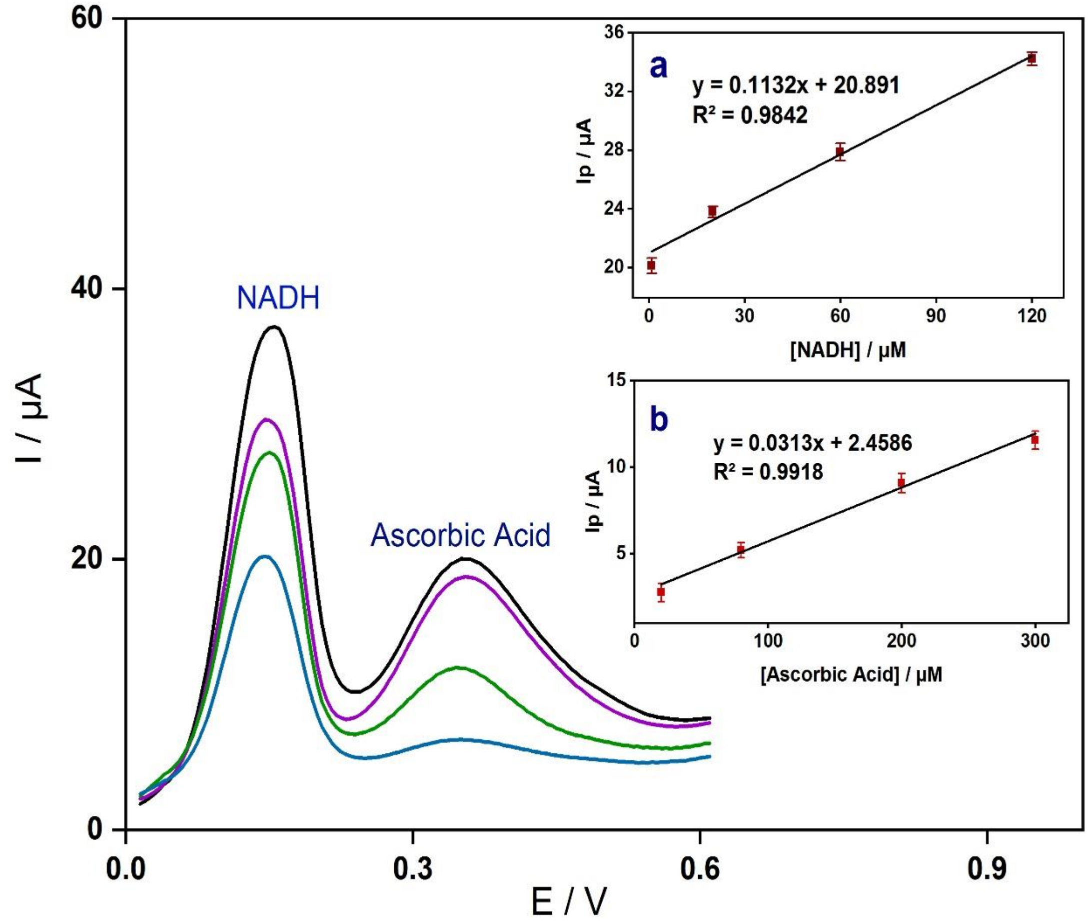

Figure S15. Differential pulse voltammograms of DBC/ZrO_2/CPE in 0.1 M phosphate buffer solution with pH = 7.0 including different concentrations of NADH + ascorbic acid in µM (1 to 4 respectively): 0.9+20.0, 20.0+80.0, 60.0+200.0, 120.0+300.0. (a) The plot of peak current versus NADH concentrations in the range of 0.9-120.0 µM, (b) The plot of peak current versus ascorbic acid concentrations in the range of 20.0-300.0 µM

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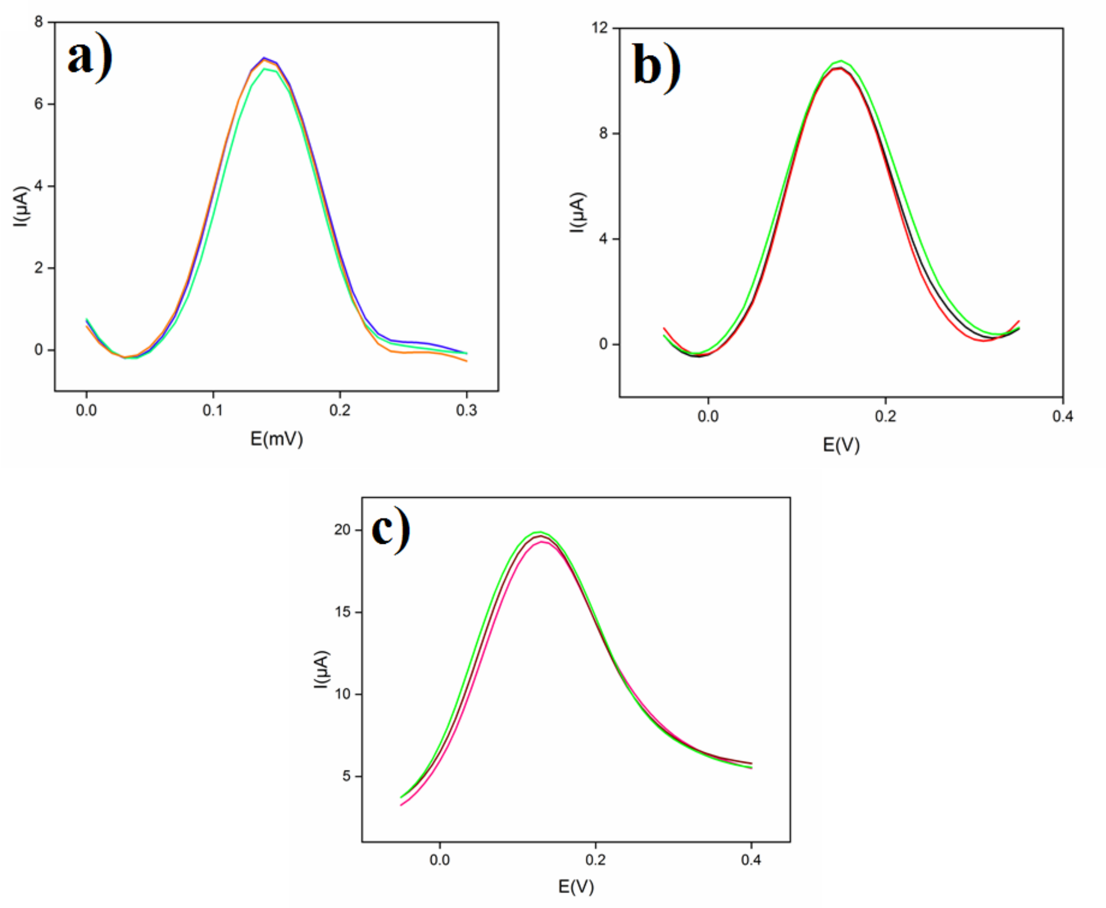

Figure S16. Differential pulse voltammogram of the DBC/ZrO_2/CPE electrode in blood serum by adding 0.2 Mμ, 0.5 Mμ and 0.9 Mμ of NADH to blood serum (a-c, respectively) at a scan rate of 50 mV s^{-1} and a potential range of 0.0-0.3 V