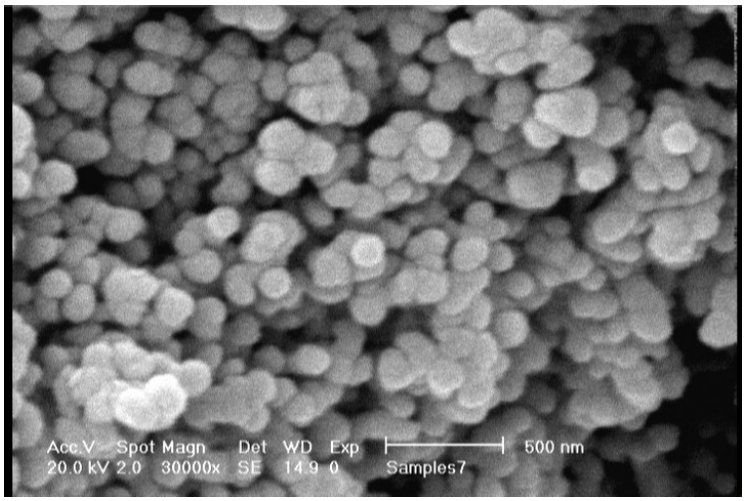
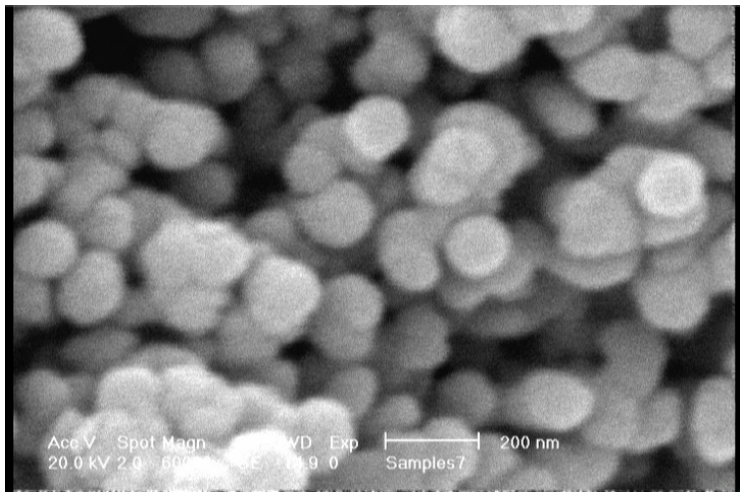
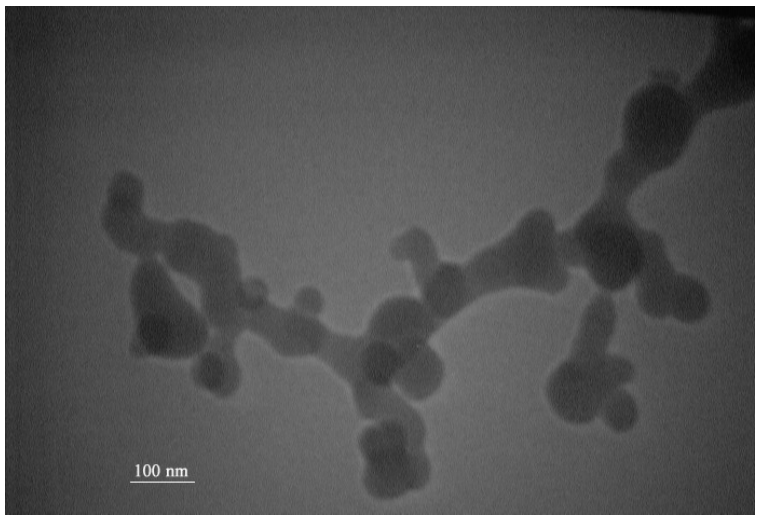
Electronic Supplementary Material (ESI) for Analytical Methods.



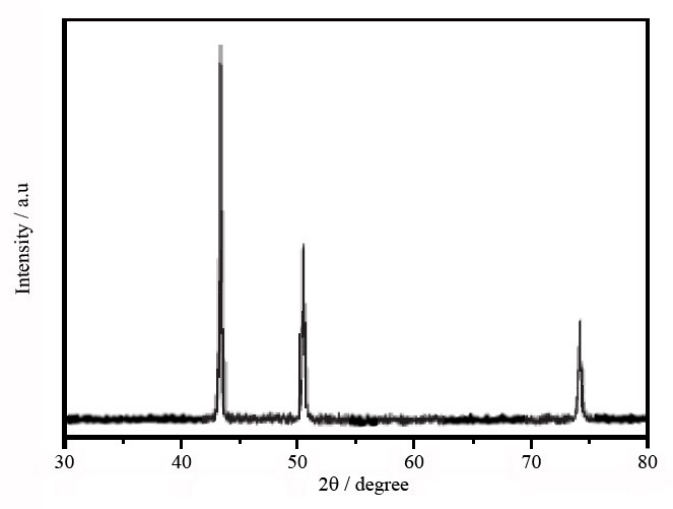
(A)



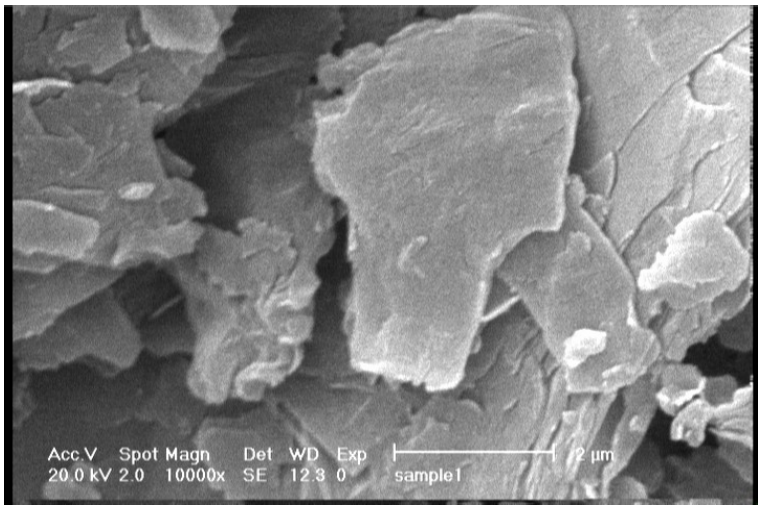
(B)



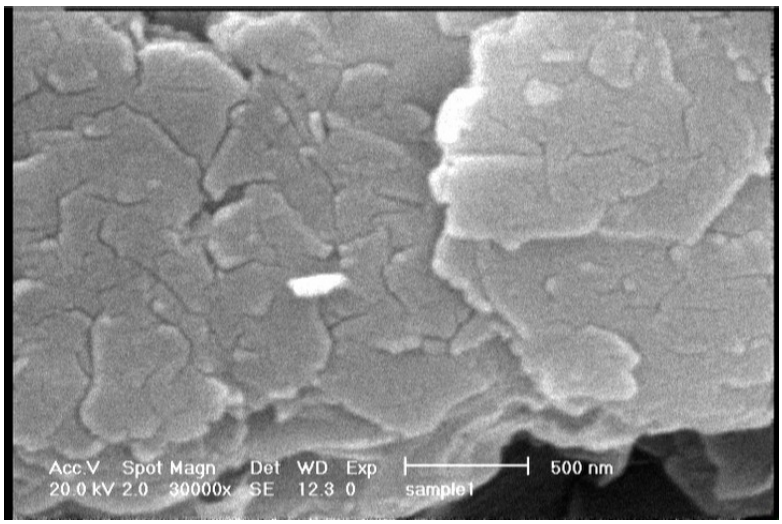
(C)


Intensity / a.u
30
40
50
60
70
80
2θ / degree

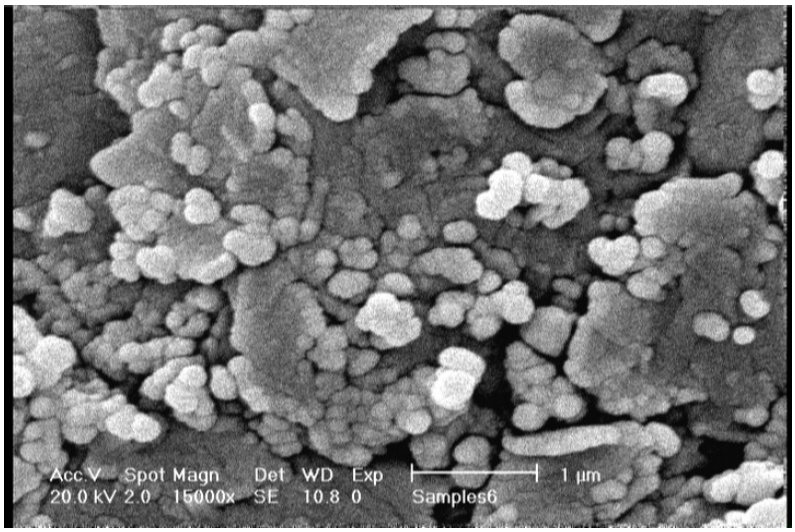
(D)


Acc.V Spot Magn Det WD Exp
20.0 kV 2.0 10000x SE 12.3 0
sample1
2 µm

(E)


Acc.V Spot Magn Det WD Exp
20.0 kV 2.0 30000x SE 12.3 0
sample1
500 nm

(F)



(G)

Figure S1: SEM and TEM images and XRD pattern of copper nanoparticles (A-D) and SEM images of graphite powder (E, F) and a paste comprised carbon microparticles and copper nanoparticles (G).

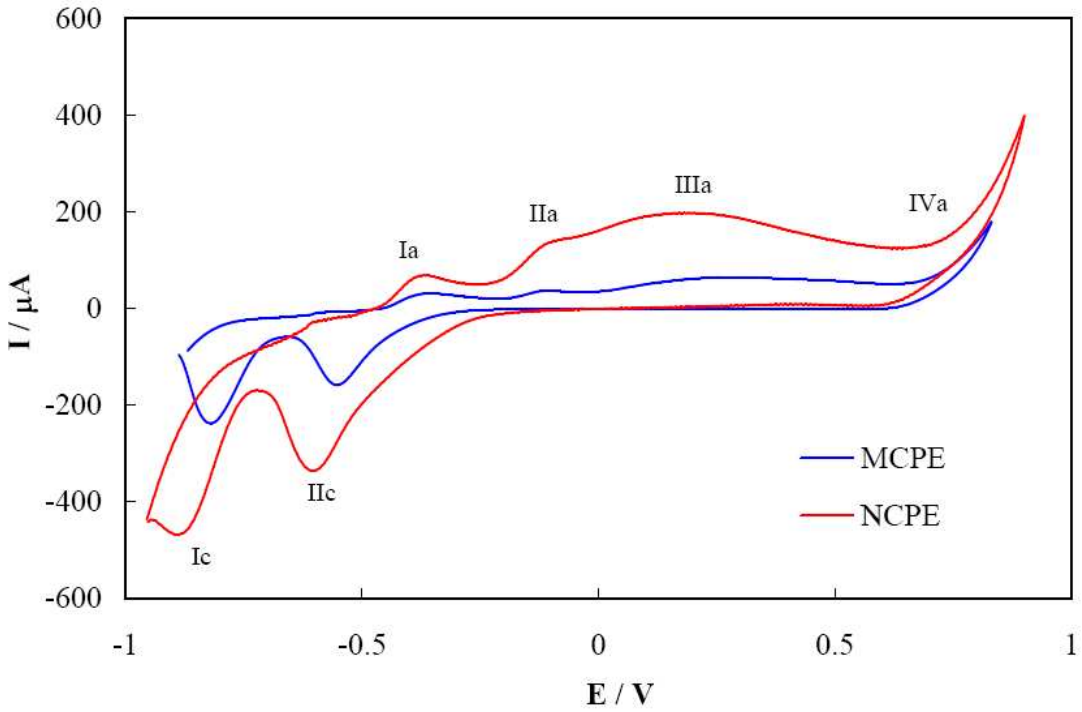


Figure S2: Typical cyclic voltammograms of MCPE and NCPE recorded in 100 mM NaOH solution. The potential sweep rate was 50 mV s^{-1}.

The voltammograms were similar and containing different peaks (I to IV). In the voltammograms, different copper species convert together [s1-s4]: peak I_a is related to the oxidation of Cu to Cu(I) species, peak II_a is related to oxidation of both Cu and Cu(I) species to the Cu(II) moiety [s4] and, peaks I_c and II_c are related to the reduction of Cu(I) to Cu and Cu(II) to Cu(I) species, respectively [s2, s5]. In addition, the anodic charge in advance of the anodic decomposition of the electrolyte is related to the Cu(II)/Cu(III) transition [s4, s6]. The redox reactions in the voltammogram can be represented as:

$$CuOH + e^- \rightleftharpoons Cu + OH^- \quad (1)$$

$$Cu(OH)_2 + 2e^- \rightleftharpoons Cu + 2OH^- \quad (2)$$

$$2Cu(OH)_2 + 2e^- \rightleftharpoons Cu_2O + H_2O + 2OH^- \quad (3)$$

$$HCuO_2^- + H_2O + 2e^- \rightleftharpoons Cu + 3OH^- \quad (4)$$

$$Cu(III) + e^- \rightleftharpoons Cu(OH)_2 \quad (5)$$

Regarding the nature of Cu(III) entity, copper oxyhydroxide and its radical (CuOO•H) have been proposed [s7, s8].

References:

[s1] H. Heli, M. Hajjizadeh, A. Jabbari, A.A. Moosavi-Movahedi, Anal. Biochem. 388 (2009) 81.
[s2] J.M. Marioli, T. Kuwana, Electrochim. Acta 37 (1992) 1187.
[s3] L.D. Burke, M.J.G. Ahern, T.G. Ryan, J. Electrochem. Soc. 137 (1990) 553.
[s4] S.M. Abd El Haleem, B.G. Ateya, J. Electroanal. Chem. 117 (1981) 309.
[s5] L.D. Burke, M.J.G. Ahern, T.G. Ryan, J. Electrochem. Soc. 137 (1990) 553.
[s6] A.M. Shams El Din, F.M. Abd El Wahab, Electrochim. Acta 9 (1964) 113.
[s7] D. Meyerstein, F.M. Hawkridge, T. Kuwana, J. Electroanal. Chem. 40 (1972) 377.
[s8] M. Fleischmann, K. Korinek, D. Pletcher, J. Chem. Soc. Perkin Trans. 2 (1972) 1396.

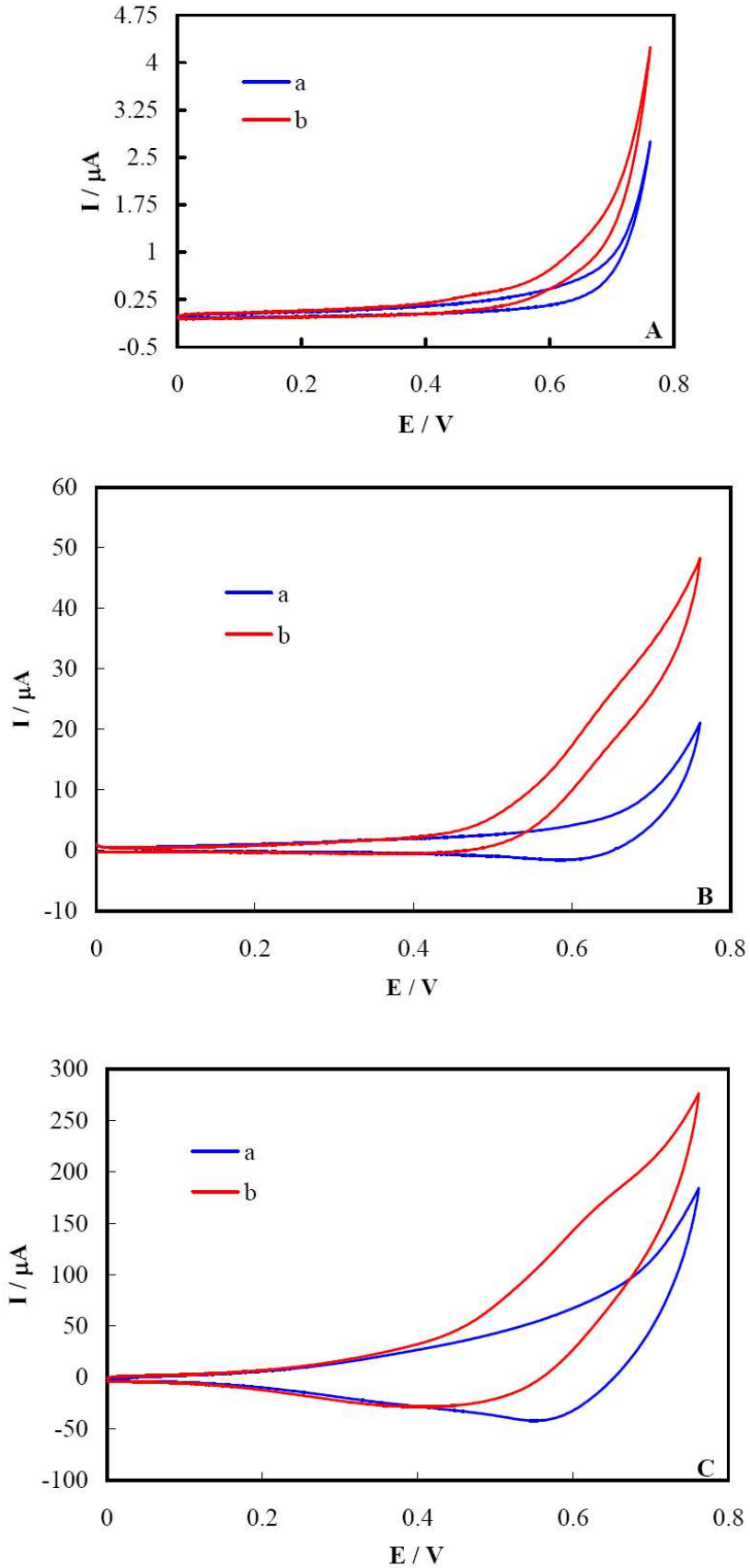


Figure S3-1: Cyclic voltammograms of UCPE (A), MCPE (B) and NCPE (C) in the absence (curve a) and presence (curve b) of 2.48 mM L-arginine. The potential sweep rate was 50 mV s^{-1}.

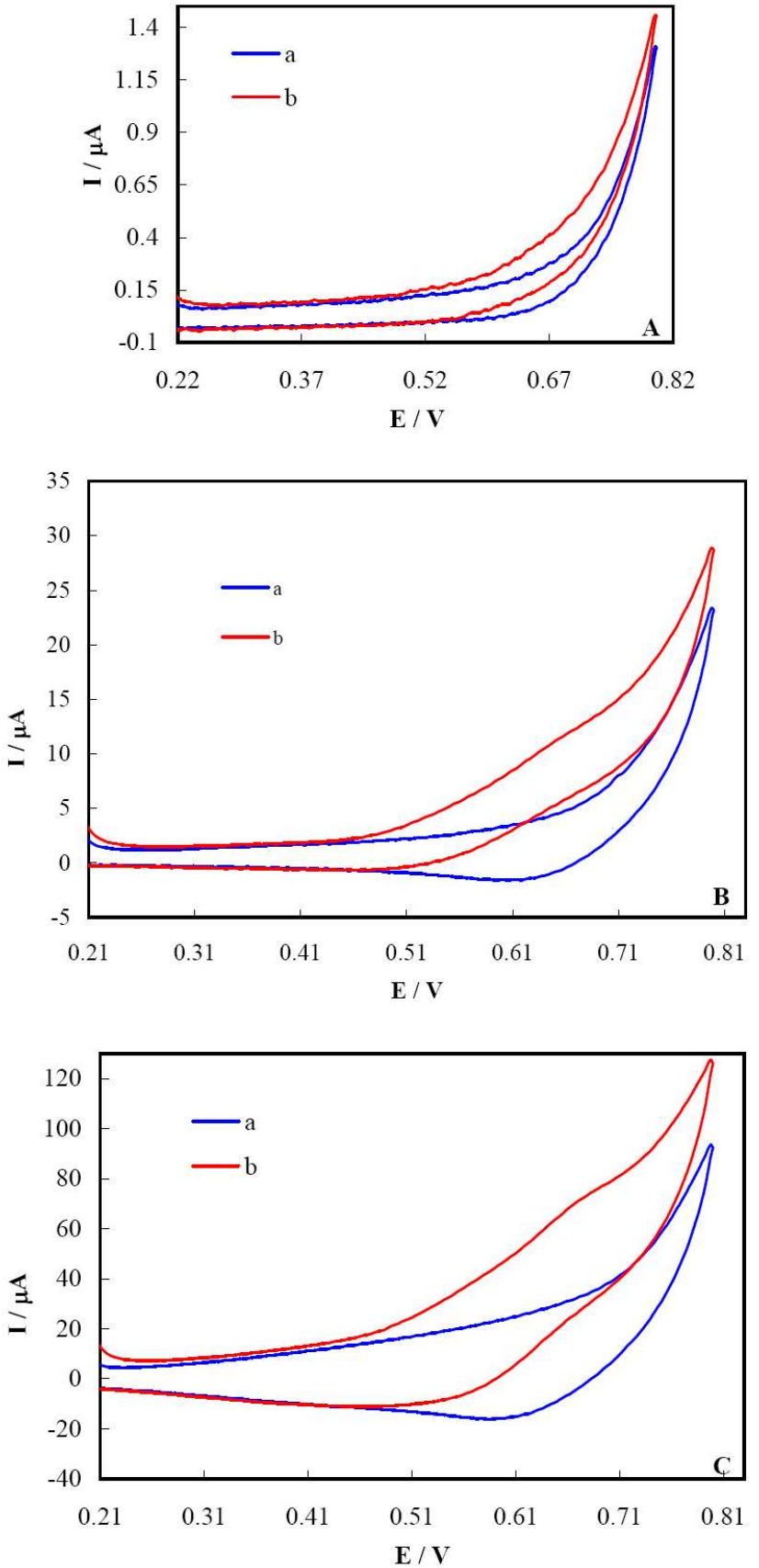
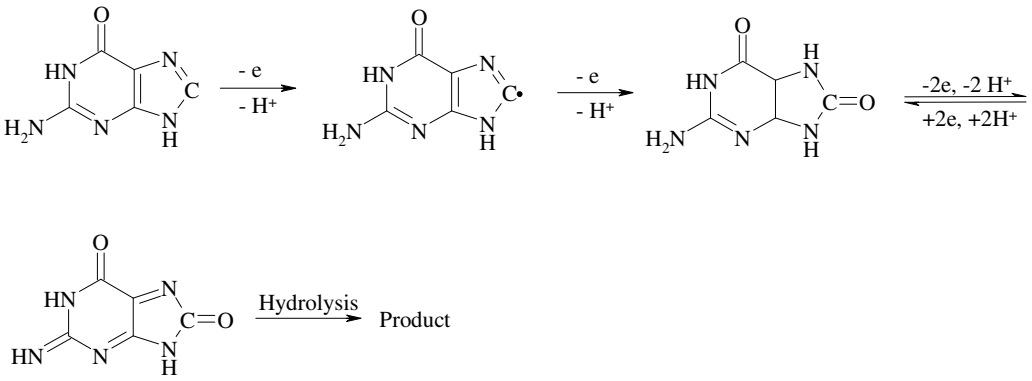


Figure S3-2: Cyclic voltammograms of UCPE (A), MCPE (B) and NCPE (C) in the absence (curve a) and presence (curve b) of 2.48 mM L-lysine. The potential sweep rate was 50 mV s^{-1}.



Scheme S4: The proposed reaction for the electrooxidation of guanine on NCPE.

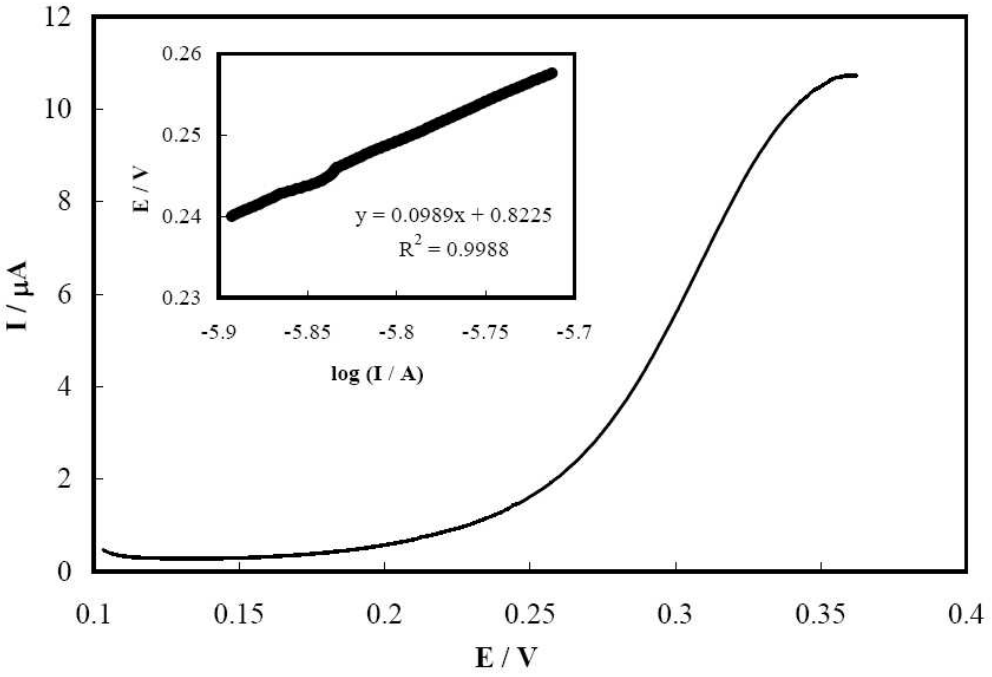


Figure S5: Steady-state polarization curves for NCPE in 100 mM sodium hydroxide in the presence of 2.48 mM guanine. Inset: The corresponding Tafel plot.