Electronic Supporting Information

Electrocatalytic Performance of a Zinc sulphide Nanoparticles modified carbon paste electrode for the simultaneous determination of acetaminophen, guanine and adenine

Mallappa Mahanthappa^{1, 2}, Nagaraju Kottam³, Shivaraj Yellappa^{1*} ¹Department of Chemistry, Government Science College, Bengaluru-560001, India ²Visvesvaraya Technological University, Research Resource Centre, Belagum-590018, India ³Department of Chemistry, M.S. Ramaiah Institute of Technology, Bengaluru-560 054, India



Fig. S1 (a) SEM images, (b) EDX pattern and (c) Elemental mapping of ZnS NPs.



Fig. S2 Zeta potential Spectrum of ZnS NPs.



Fig. S3. Effect of amount of modifier in the electrode.



Electrocatalytic activity of ZnS NPs /CPE towards oxidation of AC, G and A

Fig. S4 CVs of AC, G and A (10μM each) in 0.1 M PBS of pH 7.4 at CPE (red line) and ZnS NPs/CPE (blue line) at 50 mVs⁻¹.

Effect of scan rate

The effect of scan rate on the electrochemical response of AC, G and A at ZnS NPs /CPE in 0.1 M PBS of pH 7.4 was recorded by CV method as shown in **Fig. S4.** According to Randles-Sevcik equation, the experimental results obtained at ZnS NPs/CPE showed an increase in oxidation peak current with increase in the scan rate. As scan rate increased from 0.025 to 0.4 Vs^{-1} there was a small shifts in the peak potential with linear increase of peak current.

For the AC, linear relationship between the redox peak current and scan rate was expressed in regression equation as $I_{pa} (\mu A) = -54.835 v (Vs^{-1}) + (-1.946)$; $R^2 = 0.9819$ and $I_{pa} (\mu A) = -38.11v (Vs^{-1}) + 0.8746$; $R^2 = 0.9874$ [Inset of Fig. S4]. From the plot of log I_{pa} vs. log v, the slope value was 0.62 which was close to 0.5, this result confirmed diffusion controlled electrode process involved during experimental condition.



Fig. S5 CVs of AC, G and A (10 μ M each) in 0.1 M PBS of pH 7.4 at ZnS NPs/CPE at various scan rate (0.025 to 0.4 Vs⁻¹). (Inset of the plots of I_{pa} vs. v and I_{pa} vs. v^{1/2}).

For a reversible electrode reaction, the following Laviron's equation [38] was used to calculate the heterogeneous rate constant (k_s) ,

$$\log k_s = \alpha \log (1 - \alpha) + (1 - \alpha) \log \alpha - \log \frac{RT}{nFv} - \log \frac{\alpha (1 - \alpha) nF\Delta E_p}{2.3RT}$$
(1)

Where, k_s is the standard heterogeneous reaction rate constant; n, α , v, R, T and F represents the number of electron transferred, charge transfer co-efficient, scan rate, absolute gas constant, absolute temperature and Faraday's constant, respectively. Based on the slopes of two curves (E_{pa} vs. log v and E_{pc} vs. log v), α was calculated to be 0.52 and number of electrons (n) was 2.32 ≈ 2.0 . With the **Eq. (3)**, a value of $k_s = 1.236 \times 10^{-6} \text{ s}^{-1}$ was obtained from all the extracted experimental data.

Similarly, for G and A, linear relationship between the oxidation peak current and scan rate was expressed in regression equation for G and A as $I_{pa} = -48.504 \text{ v} (\text{Vs}^{-1}) + (-4.3834)$; $\text{R}^2 = 0.9785$ and $I_{pc} = -77.477 \text{ v} (\text{Vs}^{-1}) + (-12.0304)$; $\text{R}^2 = 0.9828$, respectively [Inset of Fig. S4]. From the plot of log I_{pa} vs. log v, for G and A, the slope values were close to 1.0, which hold good for adsorption controlled electrode process under experimental reaction condition. The peak potential shifted to more positive region on increasing of scan rate, which confirmed the irreversibility of oxidation process. A linear relationship between peak potential (E_p) and logarithmic scan rate (ln v) could be expressed by the following regression equation; G: $E_p = 0.01402 \ln v + 0.6831$; $R^2 = 0.9249$ and A: $E_p = 0.01245 \ln v + 0.9468$; $R^2 = 0.9352$.

For an irreversible electrode process, according to Laviron's [37, 39], E_p is defined by the following equation,

$$E_p = E^0 + \left(\frac{RT}{\alpha n}\right) \ln\left(\frac{RTk_0}{\alpha nF}\right) + \left(\frac{RT}{\alpha nF}\right) \ln\nu \quad (2)$$

Where, E^0 is formal potential, k_0 is the standard heterogeneous reaction rate constant and notation of other mentioned above. The value of α n could be calculated from the slope of E_p vs. In v. In this system, the slope values were calculated as 0.01402 and 0.01245 for G and A respectively, taking T = 298 K, R = 8.314 J K⁻¹ mol⁻¹ and F = 96,480 Cmol⁻¹, α n were calculated to be 1.831 and 2.064 for G and A, respectively. Generally, α was assumed to be 0.5 in a total irreversible electrode process. Therefore, the number of electrons (n) transferred during the oxidation of G and A were calculated to be ≈ 4 . The electro-oxidation of G and A at ZnS NPs/CPE were four-proton and four-electron process.



Fig. S6. DPV's of 10 μM AC, G and A in the presence of various supporting electrolytes at ZnS NPs/CPE.



Fig. S7. DPV's of 5 μM AC, G and A (a) at ten different modified ZnS NPs/CPE and (b) stability of ZnS NPs/CPE fresh & after 1 month in PBS pH 7.4.



Fig. S8. DPV's of AC, G and A content in pharmaceutical samples and hsDNA in PBS pH 7.4.