Annex

Annex 1

To calculate the electrochemistry area of an electrode has been applied Randle-Secvick equation. HOPG electrodes are cleaned (as it is described in the report) and using Potassium hexacyanoferrate (III) redox probe, different cyclic voltammetry experiments are recorded at different scan rate: 20, 50, 100, 200 and 500 $mV \cdot s^{-1}$. An example is showed below (Figure 1), where different cyclic voltammetry experiments were recorded for an electrode of HOPG:

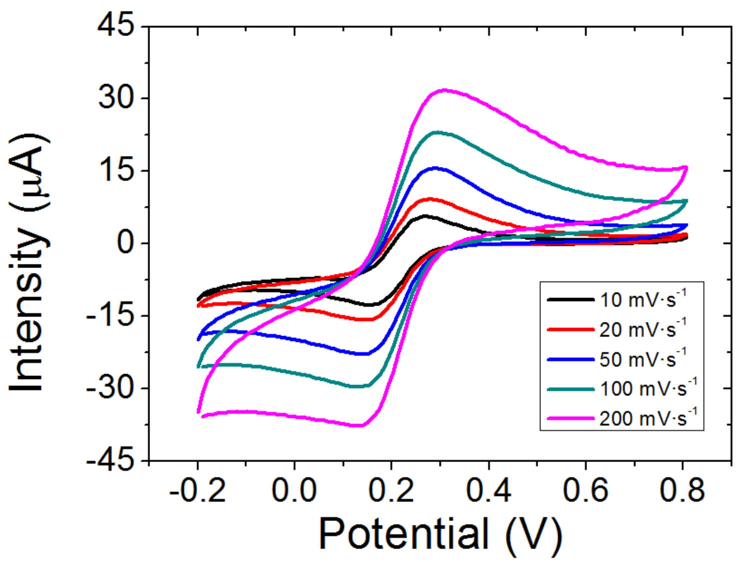

Figure 1. Cyclic voltammetry experiments of Potassium hexacyanoferrate (III) at different scan rate. KCL = 0.1 M.

Later the intensity values that correspond to anodic and cathodic peaks were represented versus the square root of the scan rate (Figure 2).

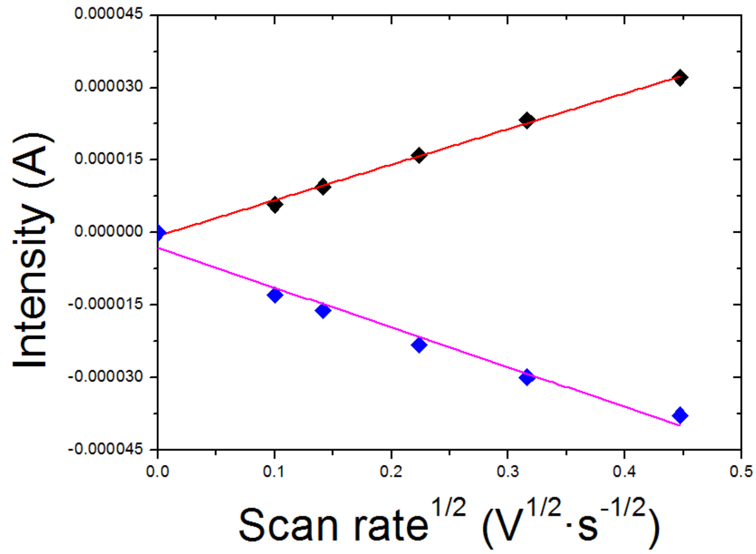

Figure 2. Anodic (pink line) and cathodic (red line) intensity peaks versus the square root of the scan rates**.**

Randle-Sevcik equation (Equation 1) in a diffusion process:

$$I_p = (2.69 \times 10^5) \times n^{\frac{3}{2}} \times A \times D^{\frac{1}{2}} \times C^b \times \nu^{\frac{1}{2}} \qquad \text{(Equation 1)}$$

Where n is the electrons transfer number by electroactive specie (Potassium hexacyanoferrate (III); n=1), A is the area of the electrode in cm^2, D is the diffusion coefficient whose value is $6.0x10^{-6}$ $cm^2\cdot s^{-1}$, C^b is the concentration of the solution in $mol\cdot cm^{-3}$ and $\nu^{1/2}$ is the scan rate in $V\cdot s^{-1}$. With these data the electrochemical area of HOPG electrodes is 0.11 cm^2

Annex 2

Redox probes are classified according to the electron transfer mechanism to the surface chemistry of an electrode. There are two principle kinds of redox probes: outer sphere and inner sphere. An outer sphere redox probe takes the electron transfer mechanism at a plane separated by at least a solvent layer from the electrode, called outer Helmholtz plane (OHP). This means that the interaction should be weak. $[Fe(CN)_6]^{3-}$ is considered outer sphere redox probes. On the other hand, an inner sphere redox probes takes the electron transfer mechanism at the surface of an electrode or materials deposited onto an electrode, at a plane called inner Helmholtz plane (IHP). Therefore the interaction should be strong and very sensitive to the surface state. Dopamine is considered inner sphere redox because it needs to be adsorbed to the surface to exchange electrons with the electrode. $[Fe(CN)_6]^{3-}$ is a large anion whose redox probe behavior depends strongly of the system, although is commonly called as outer sphere redox probe. In this case, it is necessary to analyze the system and the possible interactions of the redox probe with it. There are different electron transfer mechanisms in a system of a surface modified by *electrografting* (Figure 3) due to the presence of holes or defects:

1. In the case of $[Fe(CN)_6]^{3-}$ can give electron transfer through the layer by tunneling current. This means that the redox probe is in the OHP onto the layer and it is able to exchange electrons by tunneling with the electrode. This interaction is very weak and it needs more voltage (energy) to be produced
2. In the presence of no layer, as big holes or defects, $[Fe(CN)_6]^{3-}$ exchange electrons at the OHP directly with the electrode through the solvent layer. This interaction is stronger than case 1.
3. In the presence of no layer, as small holes or defects, $[Fe(CN)_6]^{3-}$ cannot diffuse through the holes to the surface due to repulsive electric interactions with the layer, due to having high negatively charge. In this case the redox probe cannot exchange electrons with the electrode and these small holes or defects are not detected.

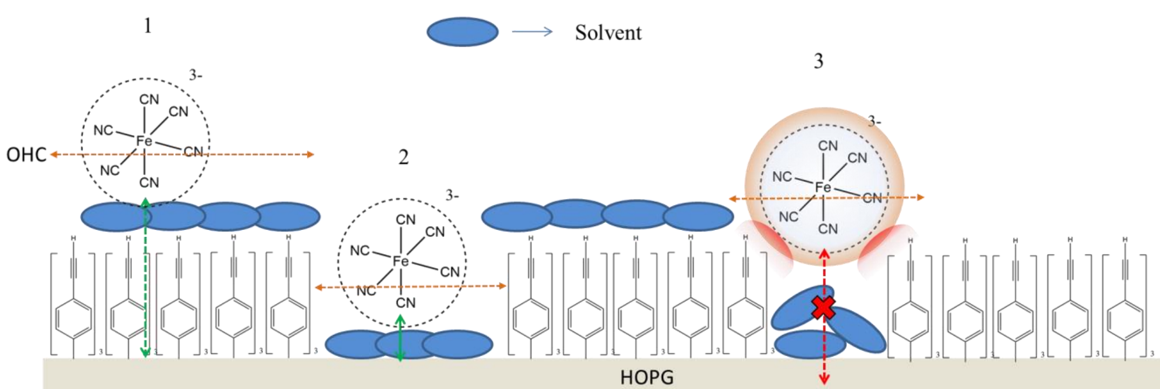

Figure 3. Electron transfer mechanism by $[Fe(CN)_6]^{3-}$ in an electrografting modification system by diazonium salts.

On the other hand, the electron transfer mechanisms for dopamine (Figure 4) are different due to the inner sphere redox probe behavior and the characteristics of the molecule:

1. As inner sphere redox probe, dopamine cannot give electron transfer by tunneling current through the layer, due to the requirement of be adsorbed onto the electrode surface to exchange the electrons.
2. In the presence of no layer, dopamine can diffuse through holes and defects easily due to be a neutral and a small molecule, as the layer. The electron transfer mechanism occurs at the close surface of the electrode, with a strong interaction between redox probe and the electrode.
3. In the presence of a no very compact layer, the molecule is small enough to diffuse through the layer and to arrive the surface, exchanging electrons with it. This electron transfer mechanism is harder than the second and it need more voltage (energy) to be produced.

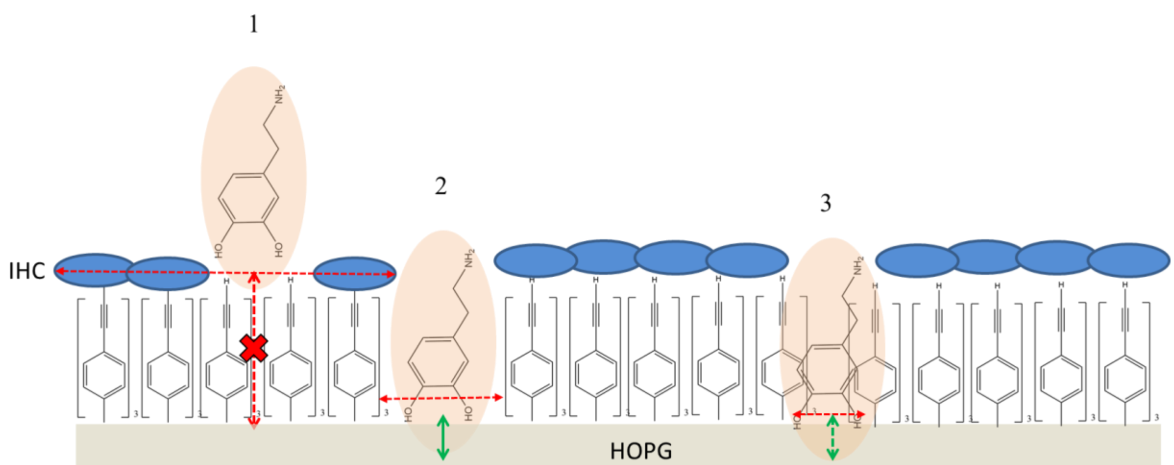

Figure 4. Electron transfer mechanism by $[Fe(CN)_6]^{3-}$ in an electrografting modification system by diazonium salts.