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#### **Presenter Information**

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## Comparative electrochemical study on the effects of heterogeneous carbon nanostructured-materials on the properties of screen-printed carbon electrodes towards Riboflavin determination

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Abstract. In this work, the influence of graphene nanoribbons (GNs), graphene nanoplatelets (GNPls), multi-walled carbon nanotubes (MWCNTs) and graphene oxide (GO) as a modifier on the properties of screen-printed carbon electrodes towards electrochemical determination of riboflavin (VB2) is investigated. Additionally, ionic liquid (IL, 1-Butyl-2,3dimethylimidazolium tetra fluoroborate), iron(II) phthalocyanine (FePc) and Nafion were added into the modifier suspensions and further tested for their electro-catalytic effect. Their performance as modifier is compared to unmodified screen-printed carbon electrodes (SPCE).Unmodified screen-printed electrodes are printed in laboratory onto the ceramic substrate using carbon ink. Modified electrodes are prepared by drop-casting modifier suspension onto the active surface area of SPCE. The three-electrode system is used, consisted of a glass vessel equipped with the screen-printed carbon electrode as a working electrode (unmodified or modified), the reference electrode an Ag/AgCl electrode (3M KCl) and the auxiliary electrode a platinum wire. The studies are done using cyclic voltammetry (CV) in Britton-Robinson buffer solution (BRBS, pH 2.0) as a supporting electrolyte at scan rate of 50 mV/s. The preliminary results show that in comparison to modified screen-printed carbon electrodes, unmodified electrodes give increased current signals where the redox reaction of riboflavin occurs. Unmodified screen printed electrodes usually give high responses due to the more hydrophilic surface and are very easy to handle, with excellent sensitivity and as low cost electro-analytical tools. Nevertheless, the results seem promising that the the modifier free sensor can be applied for the quick quantification of riboflavin.

Keywords: Riboflavin, Cyclic Voltammetry, Electrochemical Sensor, Screen-printed carbon electrode.

#### Introduction

In electrochemistry, sensors are devices that provide real-time information about the composition of an analyte. Sensors are detectors that measure the concentration of a target material by oxidizing or reducing the target material at an electrode and measuring the resulting current. In electrochemical sensors the target matter interacts with an electrolyte causing electrochemical reactions which produce a current. This current depends on the concentration

of the target material, and can be measured. They are typically based on a redox reaction involving the target analyte in the electrolyte at a working electrode, resulting in the change of an electrical signal. Well-known examples are the blood glucose sensor. Sensors are of great interest nowadays because they are easy to manufacture, integrate and use. They are cheap and detect the analyte at low concentrations. Vitamins are the important group of organic compounds and they are necessary for human health. They are required in the diet and to human body for normal growth and nutrition where their absence can lead to many diseases . Riboflavin or Vitamin B2 is a water soluble vitamin and an essential com-ponent of flavoenzymes which plays a significant role in bio-chemical reactions of the human body. It cannot be synthesized in human body therefore has to be obtained dietary from the sources such as liver, cheese, milk, meat, eggs, wines, and tea therefore its insufficiency is associated with eye lesions and skin disorders [1].

#### Objectives

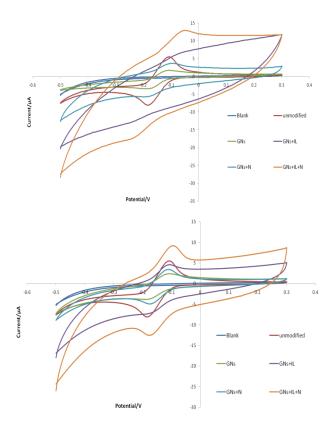
The experimental development of a sensor that would determine Riboflavin (Vitamin B2), using a carbon sensor and making various modifications with nanomaterials to the sensor in ways to increase the sensitivity of the sensor to Vit. B2. Students will also begin to have insights into the methodology of scientific research as well as begin reviewing the literature, analyzing the results, interpreting them and the full scope of research projects - to make important conclusions.

#### Materials and methods

The production of the unmodified carbon sensor is done with the semi-automatic printing machine. The manufacturing process is fast, simple and offers 30 sensors at a time, also at low cost. After printing, the ceramics are dried at room temperature and then broken into individual sensors. A silver conductive paint was applied to one side of the SPCE, the part of which is bonded for electrical contact. Carbon electrodes (SPCE) were prepared on specified ceramic substrates (Coors Ceramic, 113x166x0.635 mm aluminum plate, CLS 641000396R) with required carbon color mass (1.0 g) using a semi-automatic printing device (SP-200). , MPM, Franklin, MA, USA). The carbon sensor modifiers are then prepared. Graphene nanoribbons (GNs), graphene nanoplatelets (GNPls), multi-walled carbon nanotubes (MWCNTs) and graphene oxide (GO) were prepared in proportion 1mg/1mL in DMF and sonificated, as a modifier on the properties of screen-printed carbon electrodes towards electrochemical determination of riboflavin (VB2) is prepared. And then they are dripped into the carbon electrode modifying it depending on the modifier. Additionally, ionic liquid 0.001% and 0.5% (IL, 1-Butyl-2,3-dimethylimidazolium tetra fluoroborate), iron(II) phthalocyanine (FePc) 0.5% and Nafion 0.1% were added into the modifier suspensions and further tested for their electrocatalytic effect. Their performance as modifier is compared to unmodified screen-printed carbon electrodes (SPCE). As an electrolyte solution, the BRBS buffer was prepared as stock, whereupon it was used by adding 10 mL of it to the working container for a measurement. The stock of the Vitamin B2 0.1 mM is also prepared, where it is used by adding 1 mL to the working container for a measurement. These have been prepared with reference to the literature of previous scientific publications [1]. After separating the sensors one by one, they are modified by dropping modifiers on a 35x3mm surface of the sensor. Some sensors were drip 20  $\mu L$  of the modifier and some 5  $\mu L$  to observe the change in the result. The three-electrode system, consisting of SPCE, is used as a working electrode (unchanged or modified), the

reference electrode an Ag / AgCl electrode (3M KCl) and the auxiliary electrode a platinum wire. The working instrument, in our case the Potentiostat, is connected to the electrodes and to the other side to the computer, and controls the desired electrical potential at the three electrodes, then measures the electricity generated by the redox reaction by graphically displaying in its program on the computer. Studies were performed using cyclic voltammetry (CV) with a scan rate of 50 mV / s. Cyclic voltammetry was used as the most widely used electrochemical technique for studies in order to obtain qualitative information about the electrochemical behavior and electrochemical reactions of an electroactive species. Oxidation or reduction of an analyte can be monitored if they occur in the potential range applied, with the corresponding current peaks (anodic or cathodic peak currents, Ipa, Ipc) at a given potential (Epa, Epc) that can provide information about redox and electrochemical potentials of the analyte reaction rate. Cyclic voltammetry shows the result of current versus potential.

#### **Results and discussion**



**Fig 1**. Reaction of Riboflavin 0.1 mM with SPCE modified with GNs and other substances (high concentration of modifiers, 20 μL of modifiers are drip). **Fig. 2**. Reaction of Riboflavin 0.1 mM with SPCE modified with GNs and other substances (low concentration of modifiers, 5 μL of modifiers are drip).

In Fig. 1, the best peak is given by unmodified electrode. Measurement was done by adding higher amounts of modifiers to the working electrode.

In Fig. 2, the best peak is still given by unmodified electrode. Measurement was done by adding less amounts of modifiers to the working electrode, which improve the signal of the analyte. Also the electrode modified with GNs+N gave a good peak but not as good as unmodified one.

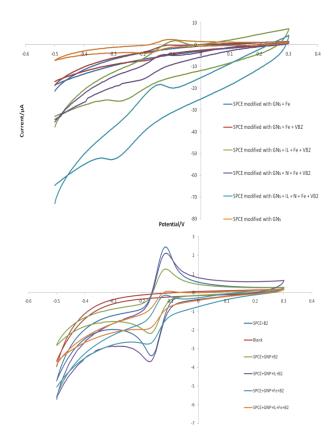


Fig. 3. Reaction of Riboflavin 0.1 mM with SPCE modified with GNs and other substances together with Fe Fig. 4. Reaction of Riboflavin 0.1 mM with GNP-modified (5 full modifier are drip). SPCE and other substances with Fe (5  $\mu$ L modifier are drip).

In Fig. 3, adding Fe as a modifier clearly aggravate the signal. In Fig. 4., SPCE modified with GNP+IL gave a good peak even the unmodified electrode gave better peaks.

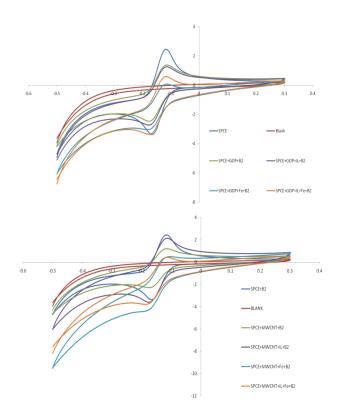


Fig. 5. Reaction of Riboflavin 0.1 mM with GOP-modified SPCE and other substances with Fe (5  $\mu$ L modifier are drip).

Fig. 6. Reaction of Riboflavin 0.1 mM with SPCE modified with MWCNT and other substances together with Fe (5  $\mu$ L modifier are drip).

In Fig. 5., SPCE modified with GOP and GOP+IL gave good peaks, but still the unmodified SPCE gave the best peak.

In Fig. 6. beside the unmodified electrode result, the electrode modified with MWCNT+IL gave also a good peak.

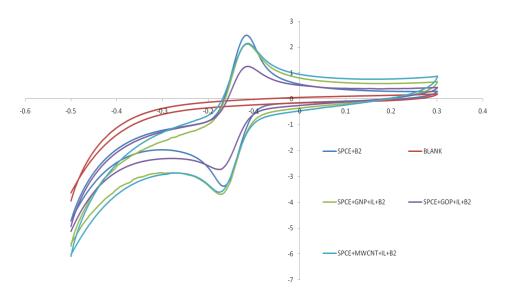


Fig 7. Comparison of the best SPCE modified with different substances results.

In Fig. 7. , the best peak is the unmodified electrode, followed by the modified electrode with GNP+IL.

#### Conclusion

The results show that in comparison, unmodified carbon electrodes give increased signals when the Riboflavin redox reaction occurs. Also with increasing concentration of modifiers at the electrode and addition of Fe as modifier resulted in inhibition of signal to Riboflavin (Fig. 1, Fig. 3). Unmodified SPCE electrodes usually give high response due to the more hydrophilic surface and are very easy to handle, with excellent sensitivity and as low-cost electro-analytical tools. The results appear promising that the unmodified sensor can be applied for rapid quantification of riboflavin.

### References

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