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Advanced Carbonized Biomass Materials for Biosensor Applications

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ADVANCED CARBONIZED BIOMASS MATERIALS FOR BIOSENSOR APPLICATIONS

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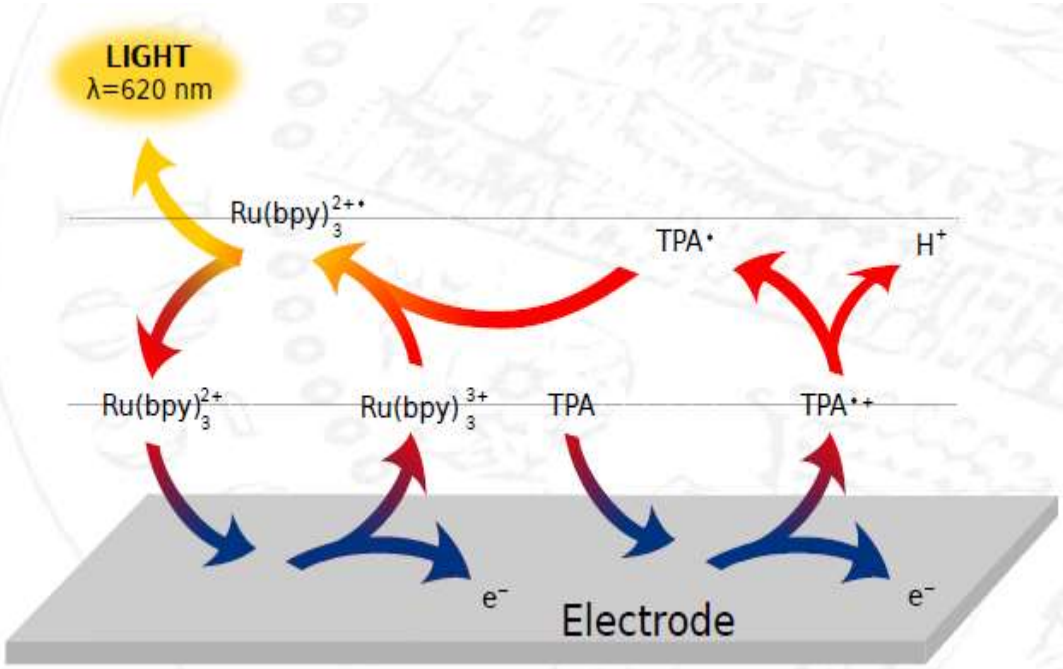
Introduction

ElectroChemiLuminescence (ECL)



Luminescence

Light Emission

Chemi-

Chemical Energy

Electro-

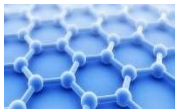
Electrochemically Initiated

REACTION

Research Motivation

- Recently there is tremendous amount of interest into green, renewable and possibly low cost bio-resources as an alternative way to produce efficient sensing elements for different kind of sensors.

- Among them, **carbon based sensors** are more attractive for the development of biosensors due to their intrinsic biocompatibility.



- ECL is a powerful electro-chemical technique that combines **high sensitivity with low cost instrumentation.**

Objective

To find the highly efficient, cheap, and environmental friendly disposable working electrode together with counter and reference electrodes for ECL based biosensor platforms.

Experimental Setup

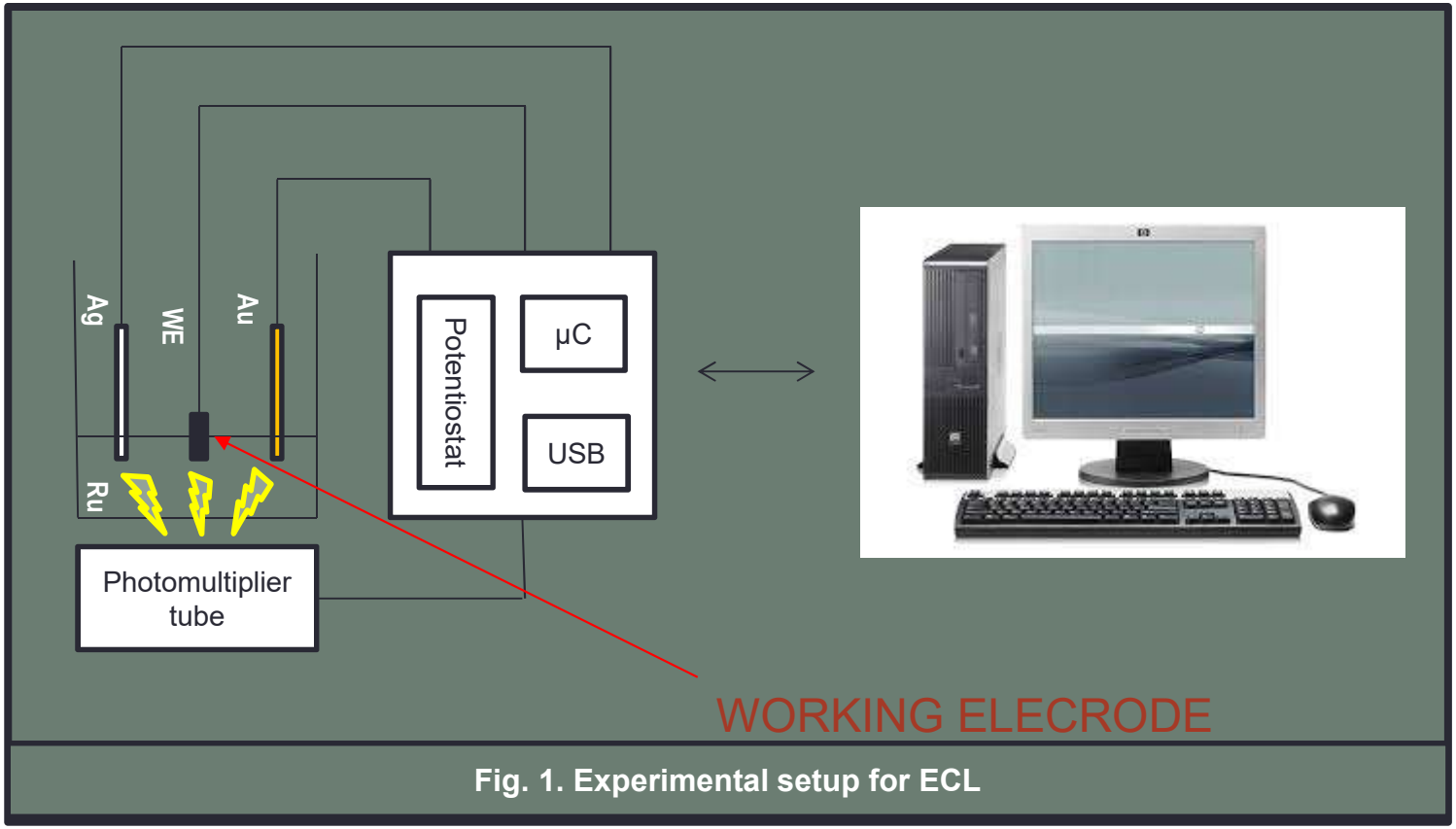
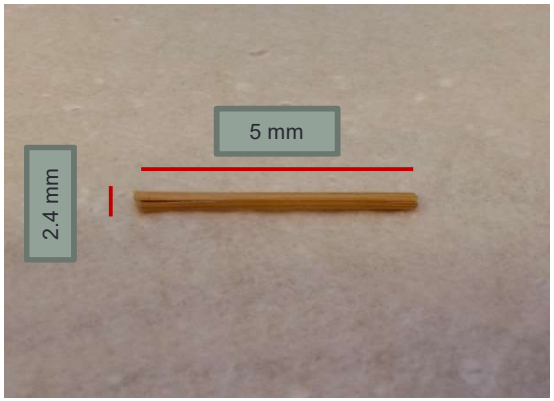


Fig. 1. Experimental setup for ECL

Synthesis

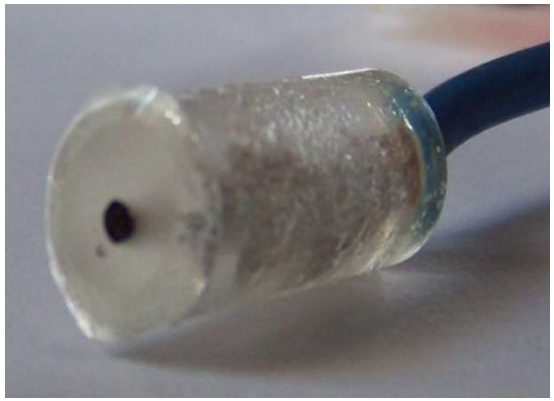
Pyrolysed Bamboo WE

Annealing **Encapsulating**



Starting material

Thermal treated material



Working Electrode

Published : M Noman, A Sanginario, P Jagdale, D Demarchi, A Tagliaferro (2014) Pyrolysed bamboo electrode for electrogenerated chemiluminescence of $Ru(bpy)^{2+}_3$. Electrochimica Acta 133:169-173. doi: 10.1016/j.electacta.2014.03.100

Activated CPNS WE

Pistachio Nut Shells

Drying

Crushing

Carbonization

Ball Milling

Char Impregnation

Activation (KOH)
Potassium Hydroxide

Pelletization

Wiring

Encapsulation

Working Electrode

Results & Comparison

Pyrolysed Bamboo (WE)

- Pyrolysed Bamboo (WE), investigated for the first time, showed a lot of promise as ECL peaks were found even with 10^{-5} M and 10^{-6} M concentration of $Ru(bpy)_3^{2+}$.
- FESEM (Fig. 3) shows the variation in the hole diameter from hundreds of nanometer to tenths of micrometer which plays an important role in ECL emission.

ECL Peaks in 10^{-4} M concentration of $Ru(bpy)_3^{2+}$

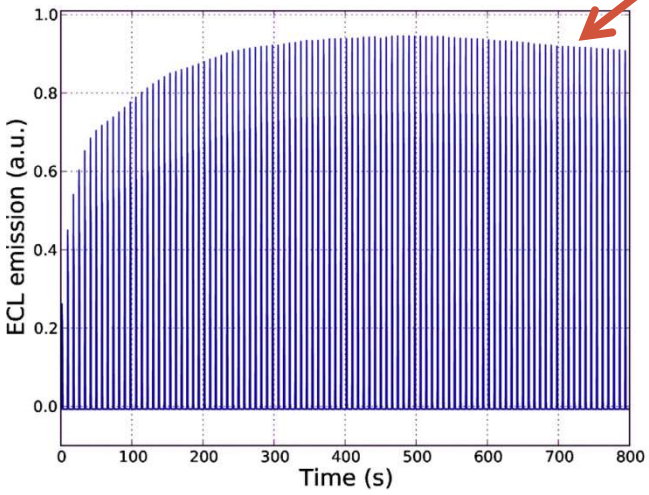


Fig. 2. ECL peaks with 1mm pyrolsed bamboo WE

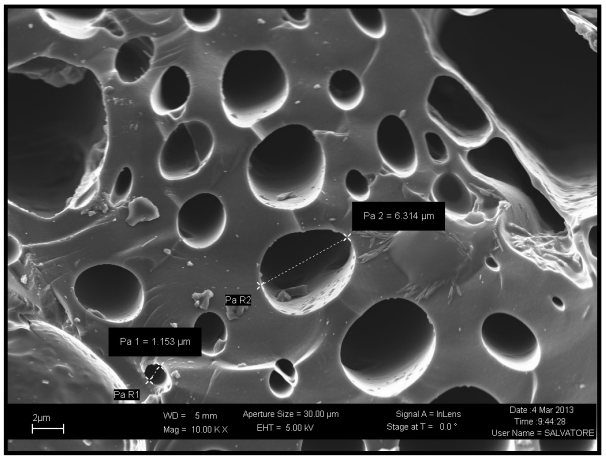
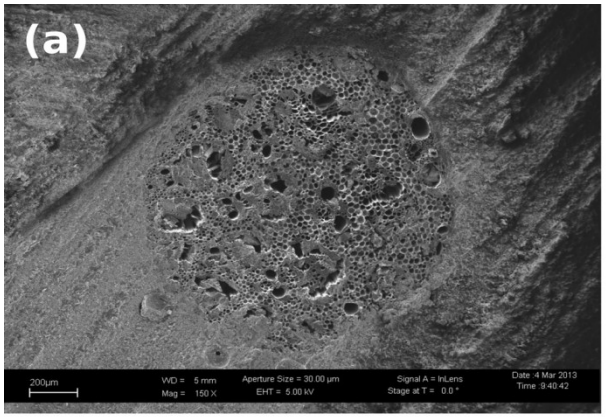
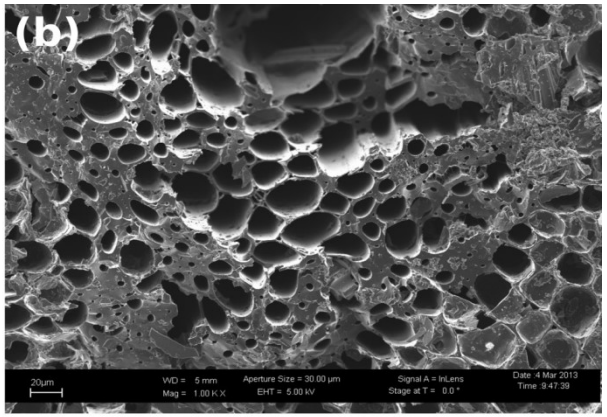
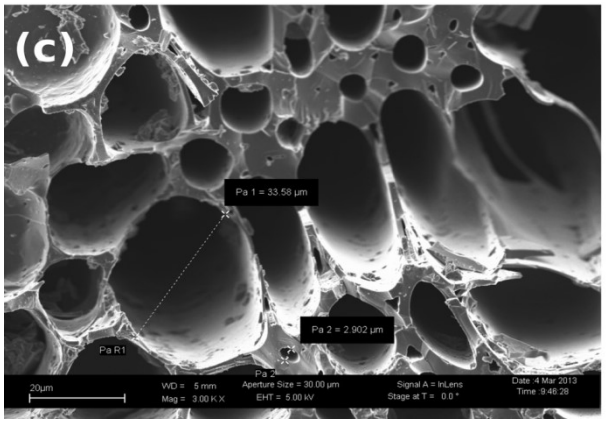


Fig. 3. FESEM image of pyrolised Bamboo

Pyrolysed Bamboo (WE)







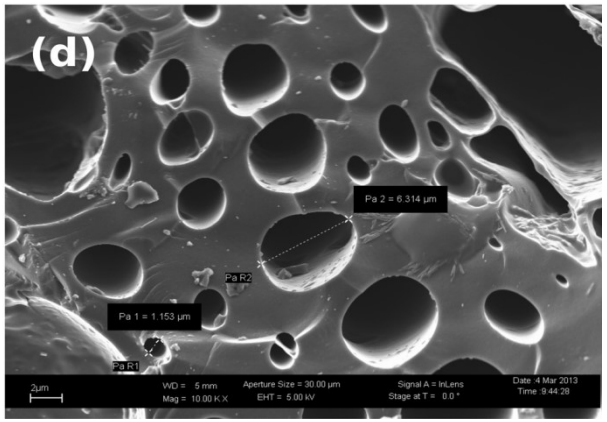


Fig. 4. SEM image of bamboo surface. (a) The whole electrode area with the surrounding epoxy resin. (b) Magnification of (a) electrode showing both empty and covered holes. (c) Part of the surface in which holes are closely packed with two measurements of a big and a small hole. (d) Part of the surface in which holes are more spaced withtwo measurements of a big and a small hole.

Pyrolysed Bamboo Characterization

- **XPS** spectrum analysis (Fig. 5) shows four photo-electronic peaks. Relative atomic concentration has been evaluated after subtracting the background noise with a Shirley function.
- According to literature the carbon peak at 284.6 eV is attributed to carbon-carbon graphitized bond while the oxygen peak at 532.9 eV is attributed to **C-O-C bond**. Remaining peaks are due to negligible amount of impurities.
- **TGA** analysis (Fig. 6) was performed in oxygen atmosphere with heating ramp rate of 10° C/min from 25-1000° C.
- Pyrolysed bamboo contains around 94% of **graphitized carbon** and its thermal stability is around 577° C meaning a high degree of purity.

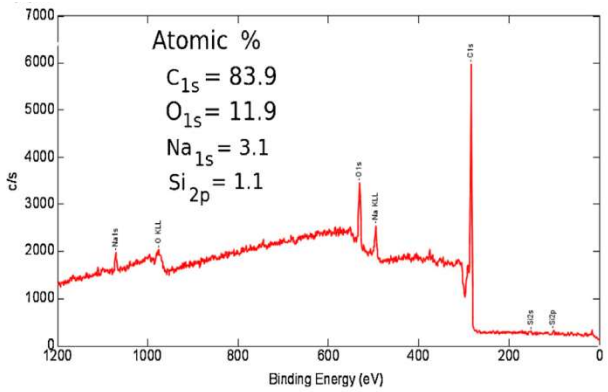


Fig. 5. XPS of pyrolysed bamboo surface

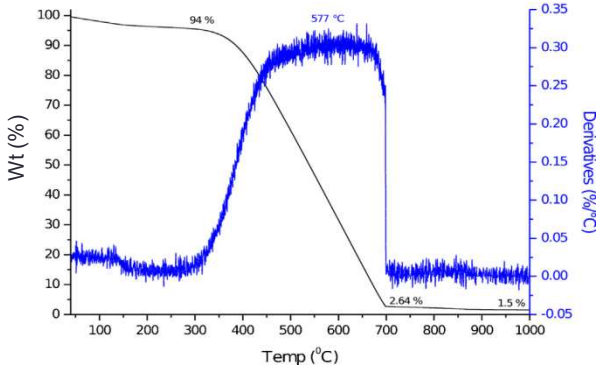


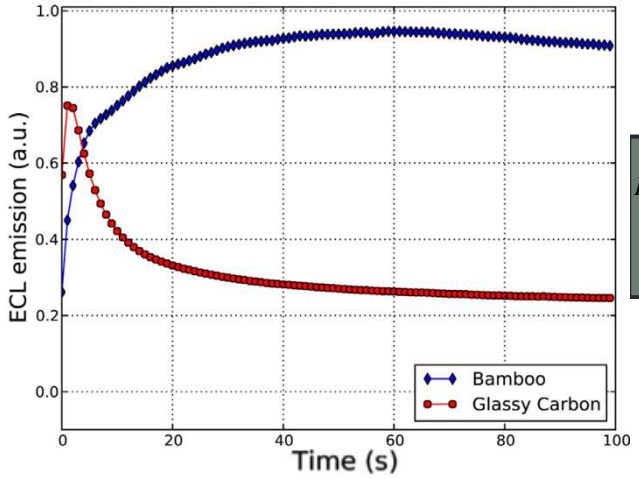
Fig. 6. TG-DTA of pyrolysed bamboo

Pyrolysed Bamboo vs Glassy Carbon

- Beside the advantage of low cost and environment friendly, pyrolysed bamboo is much **more intense** and stable in time than commercially used Glassy Carbon (GC) Electrode as shown in figure 7.

- **Reproducibility** of pyrolysed bamboo is one of the issue (Fig. 8) but one reason can be not good alignment between WE and PMT that is done manually each time. In any case, all the values are above the mean of a standard GC electrode.

- **Sensitivity, stability, low cost and environment-friendly** are the four main features which make this novel electrode even better than the existing carbon based electrodes and can provide a great platform for different kind of Biosensors in the future.



$Ru(bpy)_3^{2+}$ 10^{-4} M in PBS buffer

Scan Range: -2 V to 2 V
Scan Rate: 1 V/s

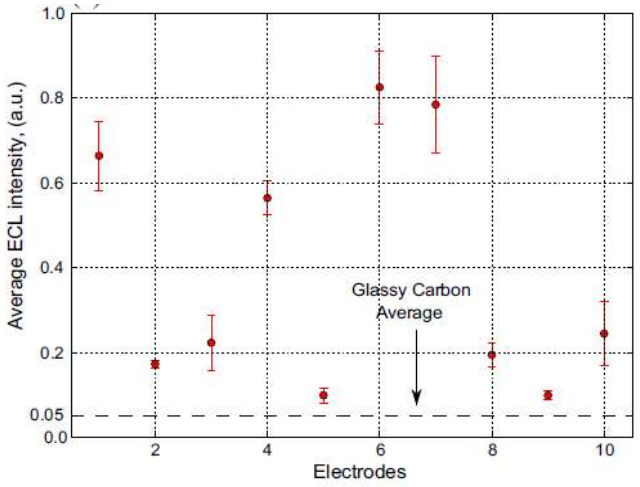


Fig. 7. Envelop of 1mm bamboo electrode signal compared with 1mm standard GC

Fig. 8. Bamboo WE reproducibility of 10 different electrodes, each tested 5 times

Activated CPNS (WE)

- Activated Carbonized Pistachio Nut Shell (CPNS), investigated for the first time, showed some good results (Not as good as Carbonized Bamboo) during ECL analysis. The emission peaks (Fig. 9) found with 3mm diameter Activated CPNS (WE) were quite stable in time.
- FESEM analysis (Fig. 10) shows the porous nature of the CPNS pellet and the presence of KOH on the surface

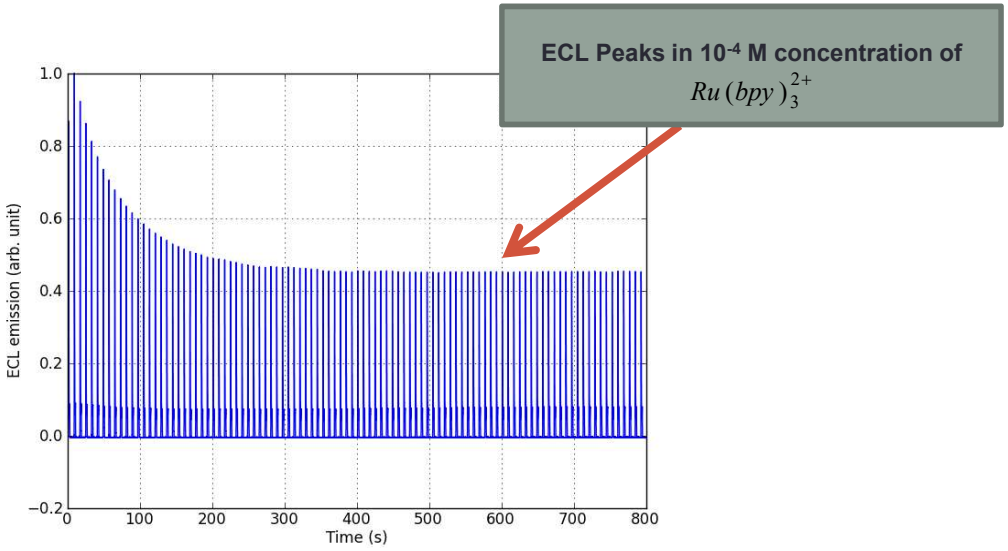


Fig. 9. ECL peaks with 3mm Activated CPNS WE

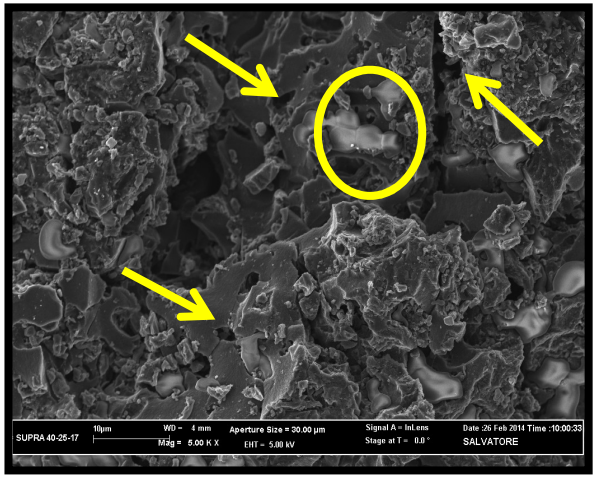


Fig. 10. FESEM image of Activated CPNS pellet

Activated CPNS (WE)

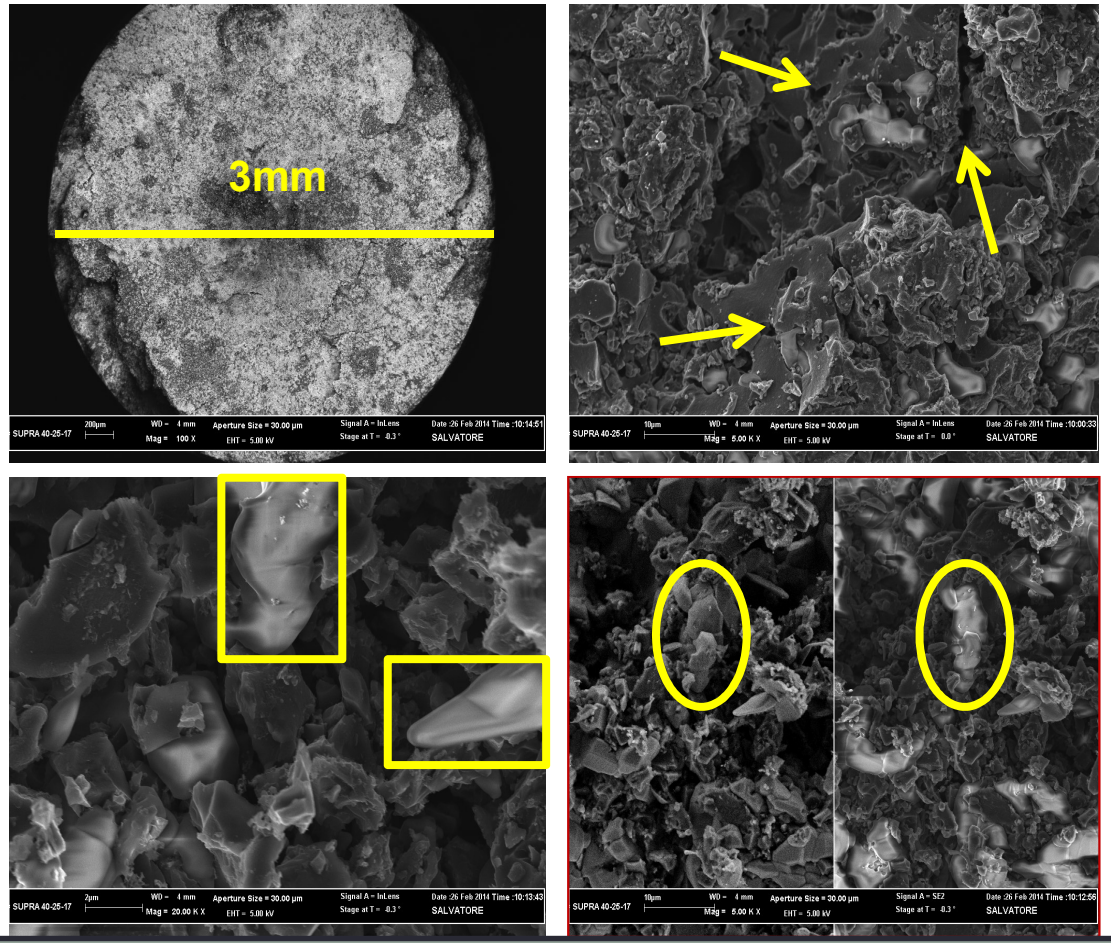


Fig. 11. FESEM analyses of (a) 3mm diameter activated CPNS electrode surface (b) pores formation after activation (c) KOH presence on the electrode surface (d) absence of metal-like reflection features in the back scattering electron image indicates that K is in its oxide form

Activated CPNS Characterization

- EDX analysis (Fig. 12) shows the presence of **Carbon** (25 %) along with **Oxygen** (43 %) and **Potassium** (32 %). The wt. % composition of K and O confirms the presence of KOH on the electrode surface.

- The TGA plot (Fig. 13) shows the thermal degradation of activated CPNS in air with a heating ramp rate of 10 ˚C/min.

- The maximum wt. loss rate is observed at 509 ^{0}C. The residual material (0.83 wt. %) is due to the presence of unreacted or thermally stable inorganic material.
- Pyrolysed bamboo contains around 94% of **graphitized carbon** and its thermal stability is around 577° C meaning a high degree of purity.

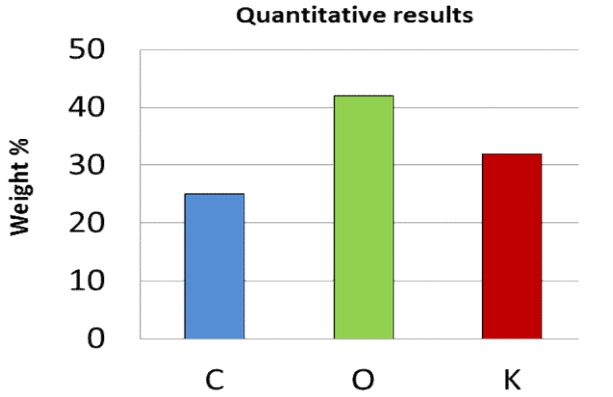


Fig. 12. EDX, Elemental wt. % composition on actvated CPNS

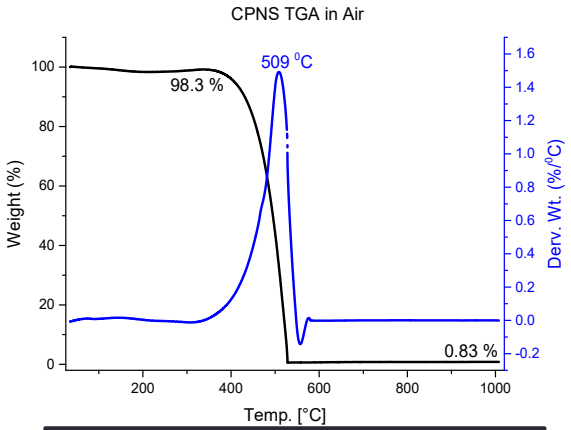


Fig. 13. TG-DTA of Actvated CPNS

Activated CPNS Vs Glassy Carbon

- Due to our apparatus limitations we can only compare 3mm Activated CPNS electrode with traditionally used 1mm GC.
- Although with higher diameter, the CPNS electroe **emission is almost similar to GC** and rather stable in time (Fig. 14)
- The final aim to reach a **low cost, environmental friendly sensor with a decent performance** has been reached.
- Like pyrolysed bamboo, it has also the issue of **reproducibility** (Fig. 15) but as discussed earlier it may be due to Not-fully accurate alignment between electrode and PMT.

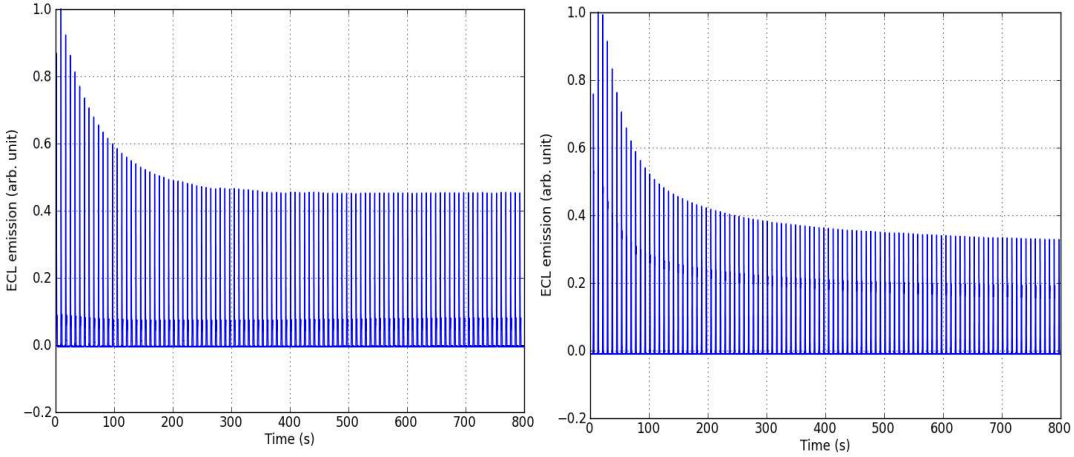


Fig. 14. ECL response of the sensor during 100 continuous voltammetry cycles. Ru (bpy) $^{2+}_{3}$ 10^{-4} M in PBS buffer at pH 7.5. Scan range: -2 V to +2 V. Scan rate 1 V/s (a) with 3mm diameter activated CPNS electrode. (b) With 1mm diameter GC electrode.

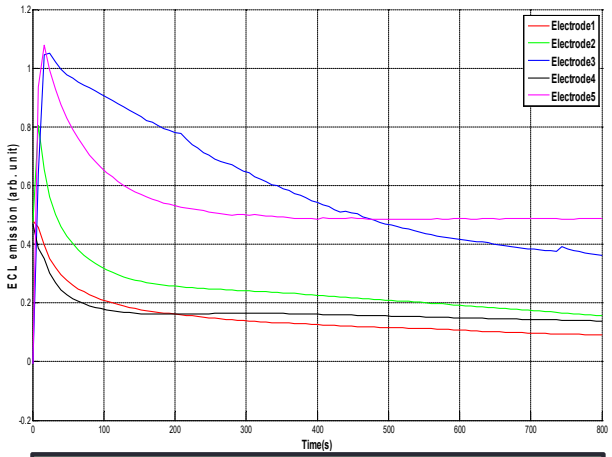


Fig. 15. Activated CPNS WE reproducibility of 5 different electrodes.

Conclusion

Conclusion

- In the present work, **a novel, low-cost and environmental friendly electrodes** for ECL has been realized starting from Bamboo and Pistachio Nut Shells.
- Experimental results demonstrated that they have outstanding electrochemical properties even if they are currently lacking of a good **reproducibility**.
- Future investigation will be performed about **detection limit, sensitivity and the role of holes** for possible **functionalization** with bio-probes for a low-cost integrated biosensors.

Thank you

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