

## SUPPORTING INFORMATION

### **Cu(II) and Hg(II) detection under photo-assisted accumulation in open circuit potential at polyazulene-EDTA like modified electrode**

Cristian Pirvu<sup>1</sup>, Gabriela Stanciu<sup>2\*</sup>, George-Octavian Buica<sup>1\*</sup>

<sup>1</sup> Faculty of Chemical Engineering and Biotechnologies, University Politehnica of Bucharest, 1-7 Gheorghe Polizu St, Bucharest, 011061, Romania

\*buica\_george@yahoo.com

<sup>2</sup> Department of Chemistry and Chemical Engineering, Ovidius University, 124 Mamaia Blvd, Constanta, 900527, Romania

\*gstanciu66@yahoo.com

## **Experimental**

### *Materials and reagents*

The ligand 2,2'-(Ethane-1,2-diylbis((2-(azulen-2-ylamino)-2-oxoethyl)azanediyl))diacetic acid (**L**) was obtained following a procedure previously described [1]. The ligand was electropolymerized according to the previous procedure [2]. Briefly, the glassy carbon (GC) discs (Orignalys, 6 mm diameter) were modified with poly**L** films under imposed potential using an electric charge of 3 mC (unless otherwise stated). GC electrodes modified with poly**L** films (further denoted GC|poly**L**) were obtained from a solution of **L** (1.5 mM) + 2 molar equivalents of HNO<sub>3</sub> in 0.1 M tetrabutylammonium perchlorate (TBAP, Sigma Aldrich, electrochemical analysis grade) and acetonitrile (ACN, Sigma Aldrich, 99.999%) using Ag|10mM Ag<sup>+</sup>, 0.1M TBAP, ACN and Pt mesh as reference and auxiliary electrodes, respectively. After electropolymerization, GC|poly**L** electrodes were carefully washed with acetonitrile and stored in sealed sterile tubes until further use.

### *Equipments*

The electrochemical impedance spectroscopy (EIS) and Mott-Schottky experiments were performed on IVIUM pocketSTAT2.LC potentiostat. All other electrochemical assays were conducted on the AUTOLAB PGSTAT 204 potentiostat. The Ag|AgCl, 3M KCl system (Metrohm) was considered as a reference electrode and Pt was used as an auxiliary electrode for electrochemical procedures performed aqueous phase.

A Millipore Direct Q 3UV from Merck,  $18.2 \text{ M}\Omega \text{ cm}^{-1}$  system was used as a source of purified water, which was subsequently used as a solvent in the preparation of all aqueous solutions.

The pH of acetate buffer solutions was measured with a WTW InoLab 7110 pH meter and a dual lamp (254nm and 365nm) from Ultra-Lum model UVAC-16, Ultra-Lum, Inc., was used as a source of irradiation.

### *Procedures*

Before the metal ions accumulation step, the GC|polyL modified electrode was transferred in metal free 0.1M acetate buffer and equilibrated by performing 15 successive voltammetric cycles in the potential range of  $-0.9\text{V} - 0.5 \text{ V}$ . During successive cycling, the GC|polyL electrode present an oxidation-reduction behaviour and it shows a stable behaviour (Figure S1).

The metal ions accumulation on GC|polyL electrodes was performed in open circuit potential under photoirradiation. The electrode was placed into a quartz cuvette containing 25 mL 0.1M acetate buffer and Zn(II), Cd(II), Pb(II), Cu(II), and Hg(II) ions. Following accumulation, the reduced metal ions on the GC|polyL surface were re-oxidized to metal ions by anodic stripping using the differential pulse voltammetry (DPV) technique ( $20 \text{ mV s}^{-1}$ , 25 mV amplitude, and 0.5 s pulse periods).

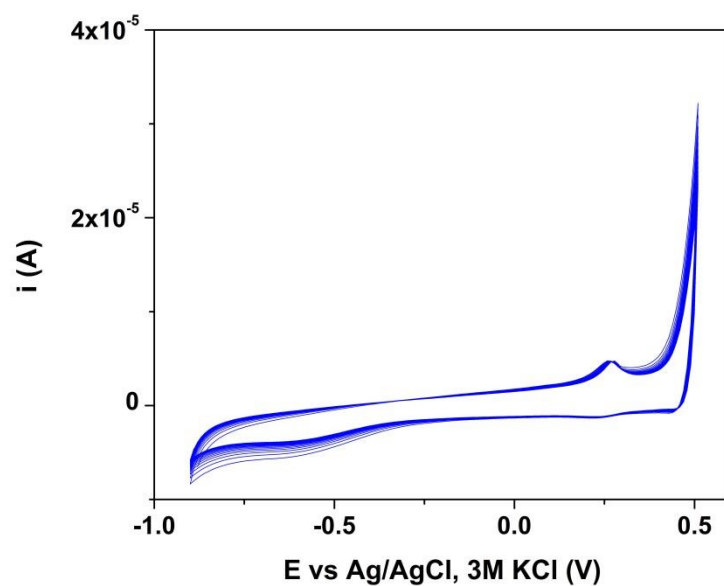


Fig. S1. Successive CV curves for GC|polyL modified electrode in 0.1M acetate buffer.

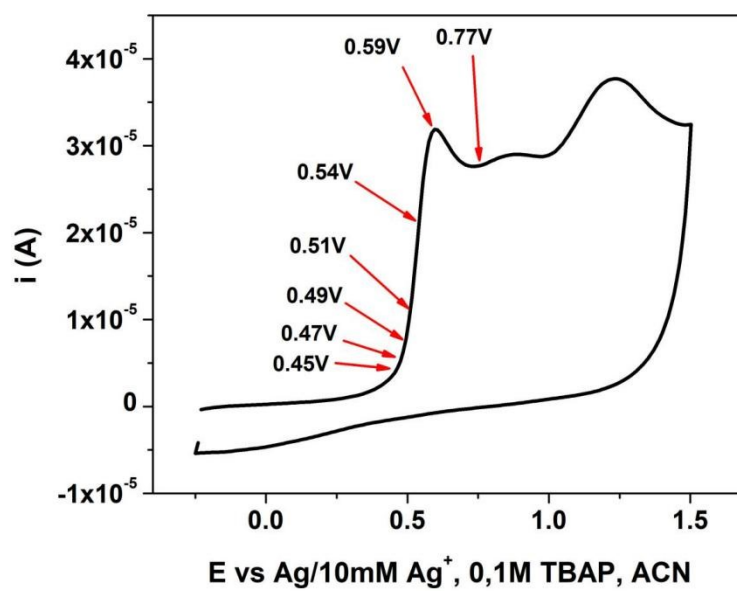


Fig. S2. CV curve (0.1 V/s) on GC electrode (3 mm in diameter) for L [1.5mM] in 0.1 M TBAP, ACN.

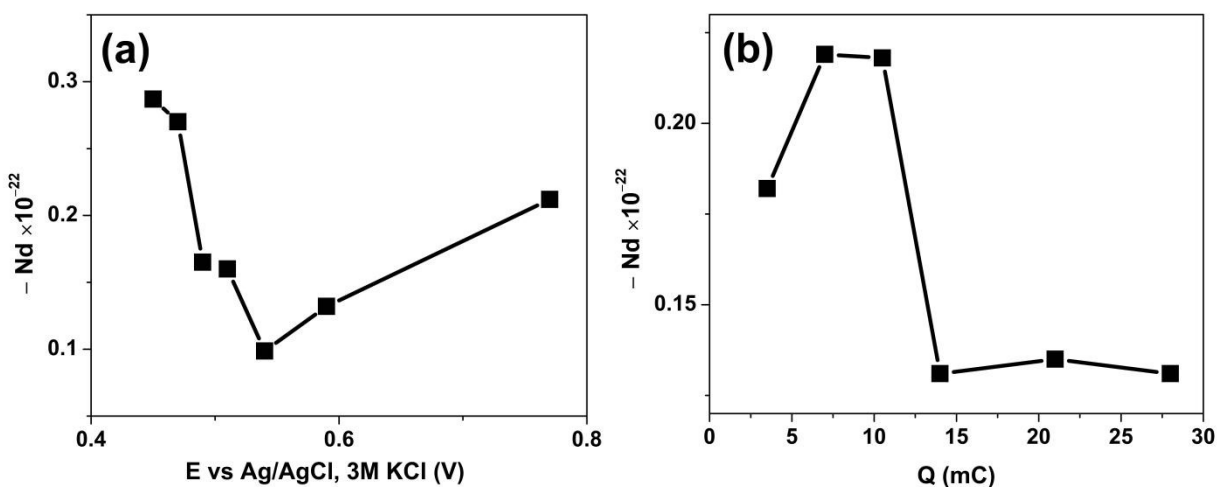


Fig. S3. The carrier charge density ( $Nd$ ) for different GC|polyL modified electrodes obtained at (a) different polymerization potentials ( $Q = 7 \text{ mC/cm}^2$ ) and (b) at different polymerization charge ( $E = 0.51 \text{ V}$ ).

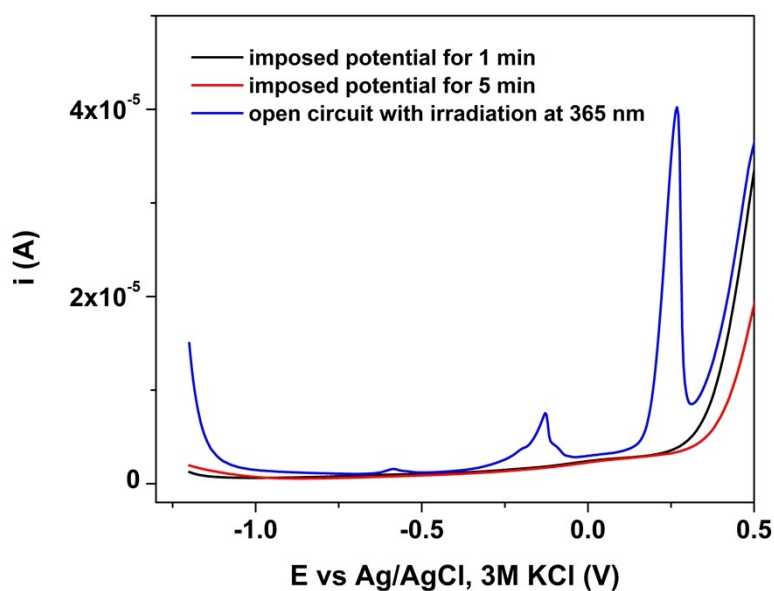


Fig. S4. DPV curves ( $20 \text{ mV s}^{-1}$ ,  $25 \text{ mV}$  amplitude, and  $0.5 \text{ s}$  pulse periods) recorded on GC|polyL electrodes after accumulation under imposed potential ( $E = -1.2 \text{ V}$ ) and in open circuit with UV light irradiation. Metal ions accumulation was performed in  $0.1 \text{ M}$  acetate buffer ( $\text{pH} =$

4) which contain  $5 \times 10^{-7}$  M of Zn, Cd(II), Pb(II), Cu(II), and Hg(II) for 1 and 5 min under imposed potential and 30 min in open circuit with UV light irradiation.

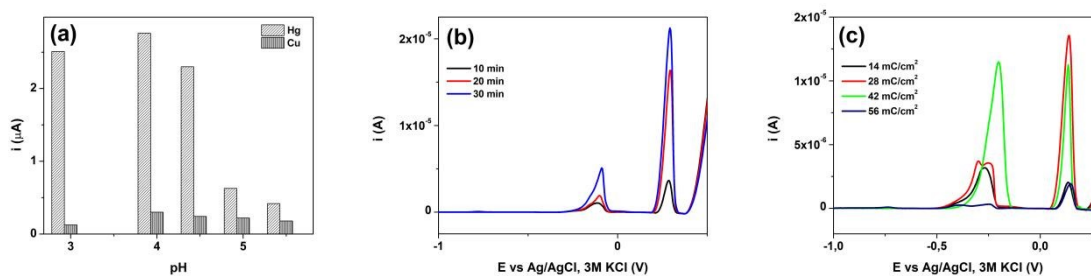


Fig. S5. Influence of (a) pH, (b) accumulation time under UV light irradiation, and (c) amount of electric charge used in the polymerization process on the sensing properties of GC|polyL electrodes.

Table S1. Electrical fitted parameters of the equivalent circuit for C|polyL modified electrodes obtained by CPE at different polymerization potentials (CPE) and electric charges (Q).

CPE (V) / Q (mC/cm <sup>2</sup> )	R1 (Ohm)	R2 (Ohm)	Q1 (s <sup>N</sup> /Ohm)	N1	R3 (Ohm)	Q2 (s <sup>N</sup> /Ohm)	N2
0.45	8.806E+01	9.881E+02	7.417E-09	9.452E-01	5.081E+05	4.309E-06	8.338E-01
0.47	8.596E+01	9.769E+02	8.529E-09	9.217E-01	1.841E+05	3.105E-06	8.760E-01
0.49	8.826E+01	9.785E+02	8.682E-09	9.298E-01	2.650E+05	2.934E-06	8.632E-01
0.51	8.400E+01	9.469E+02	7.139E-09	9.677E-01	1.841E+05	3.487E-06	8.387E-01
0.54	7.394E+01	8.425E+02	1.017E-08	9.339E-01	3.316E+05	2.699E-06	8.428E-01
0.59	7.776E+01	8.354E+02	9.884E-09	9.373E-01	5.339E+05	2.564E-06	8.558E-01
0.77	5.264E+01	7.766E+02	1.566E-08	9.042E-01	5.586E+06	2.072E-06	8.931E-01
3.5	1.178E+02	8.669E+02	5.612E-09	9.704E-01	1.506E+06	4.000E-06	8.112E-01
7	8.647E+01	7.191E+02	9.061E-09	9.463E-01	2.011E+05	3.302E-06	8.553E-01
10.5	1.089E+02	8.767E+02	5.617E-09	9.648E-01	1.512E+05	4.382E-06	8.238E-01
14	1.075E+02	8.470E+02	5.266E-09	9.705E-01	1.023E+05	4.162E-06	8.070E-01

---

21	1.100E+02	8.533E+02	6.124E-09	9.596E-01	1.250E+05	4.034E-06	8.247E-01
28	8.495E+01	7.309E+02	6.683E-09	9.703E-01	1.007E+05	4.537E-06	8.019E-01

---

## References

1. G.-O. Buica, I.-G. Lazar, L. Birzan, C. Lete, M. Prodana, M. Enachescu, V. Tecuceanu, A.B. Stoian, E.-M. Ungureanu, *Electrochimica Acta*, 2018, **263**, 382–390.
2. G.-O. Buica, A. A. Ivanov, I.-G. Lazar, G.-L. Tatu (Arnold), C. Omocea, L. Birzan, E.-M. Ungureanu, *J. Electroanal. Chem.*, 2019, **849**, 113351.