## **Electronic supplementary information**

## Electrode modified with nanoparticles composed of 4,4'bipyridine-silver coordination polymer for sensitive determination of Hg(II), Cu(II) and Pb(II)

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**Table S-1**. Electrochemical parameters obtained by fitting EIS data in the successive steps of preparation. ( $R_s$ —solution resistance,  $R_{ct}$ —charge transfer resistance, Q-constant phase element, W- warburg impedance).

Modification step	$R_{\rm s}\left(\Omega\right)$	$R_{\rm ct}$ (k $\Omega$ )	$W(\mu S)$	$Q$ ( $\mu$ S/n)
Bare GCE	106	0.064	295	6.35 / 0.811
PNB/GCE	70.5	7.26	181	3.75 / 0.741
Ag/PMB/GCE	75.4	6.13	282	3.16 / 0.769
Ag-bipy-CP/PMB/GCE	84.3	4.31	251	1.69 / 0.865

GCE- glassy carbon electrode, PMB- phenylmethyl-4,4'-bipyridinium, bipy- 4,4'-bipyridine, CP- coordination polymer

**Table S-2.** Analytical performance of Ag-bipy-CP/PMB/GCE in comparison with varioussensors for Hg (II), Cu (II) and Pb (II) analysis

Modified electrode	Analyte	Peak potential [V]	Linear range [µg L <sup>-1</sup> ]	LOD [µg L <sup>-1</sup> ]	RSD %	Obs.	Ref.
SPE modified with	Pb (II)	-0.567	8.3 -41.4	4.76	4.5	electrodes	
mercury nano-droplets	Cu (II)	-0.270	2.52 -12.6	0.75	3.0	can not be reused	[1]
CPE modified with chitosan nanoparticle- Schiff base	Pb (II)	-0.35	207-20700	149.8	-	interferences from $Cu^{2+}$ , $Cd^{2+}$	[2]
ITO electrode modified with 5-methyl-2- thiouracil, graphene oxide and gold nanoparticles	Hg (II)	0.74	1 - 22	0.15	3.3	only one analyte	[3]
GCE modified with	Cu (II)	0.31	315 - 945	0.63	4.3	was not	[4]
hierarchical gold dendrites	Pb (II)	-0.09	1035 - 3105	2.07	2.7	applied in real samples	
SPE modified with gold films, and metal ion	Hg (II)	0.4	2 - 16	1.5	3		[5]
preconcentration with thiol-modified magnetic particles	ncentration iol-modified Pb (II) etic particles	-0.28	4-16	0.5	6		[~]
Gold electrode	Pb (II)	-0.11	0.11 .32 1-100	0.16	4.5		
modified with Au	Cu (II)	0.32		0.15	3.9		[6]
nanoparticles	Hg (II)	0.56		0.14	4.9		
CPE modified with a palladium oxide supported onto natural phosphate	Hg (II)	0.13	50-20000	3.86	4.78	_	[7]
A boron-doped diamond nanocristaline thin-film	Pb (II)	-0.55	1-10	0.98	3.5	was not applied in real samples	[8]
A hanging mercury drop electrode activate with nano-Al <sub>2</sub> O <sub>3</sub>	Pb (II)	-0.38	0.01-100	0.0046	2.83	-	[9]
CPE modified with diethylenetriamine pentaacetic acid functionalized Fe <sub>3</sub> O <sub>4</sub> magnetic nanoparticles	Cu (II)	-0.1	0.31 - 6350	0.13	5.3	was not applied in	[10]
	Pb (II)	-0.45	103.5 - 207000	1.69	4.9	real samples	
GCE modified with nanoparticles composed of Ag-bipy-CP	Hg (II)	+0.3	0.2 - 10	0.09	3.2		this
	Cu (II)	-0.07	1.3 - 6.4	0.71	4.5	_	work
	Pb (II)	-0.54	4.2 - 20.7	2.3	3.9		<u> </u>



**Figure S-1**. Comparison of recorded crystal structure analysis for the Ag-bipy-CP (a) and simulated ZIJGUU structure (b)



Figure S-2. FT-IR spectra of (a) 4,4'-dipyridine and (b) Ag-dipy-CP



Figure S-3. TEM images of Ag-dipy-CP



**Figure S-4**. Response of GCE modified electrode as a function of accumulation time. Accumulation conditions:  $1 \ \mu g \ L^{-1} \ Hg (II)$  in acetate buffer (pH=5.0) at - 0.6V.



Figure S-5. Influence of the deposition potential on the modified electrode surface to the registered analytical signal of  $1 \ \mu g \ L^{-1} \ Hg (II)$ .



Figure S-6. Effect of the pH on the stripping peak current of 1  $\mu$ g L<sup>-1</sup> Hg (II) using Ag-bipy-CP/PMB/GCE



**Figure S-7.** Differential pulse voltammograms recorded for GC-modified electrode and calibration plots obtained for Pb (II) concentrations: 4.1; 6.2; 8.3; 12.4; 16.5 and 20.7  $\mu$ g L<sup>-1</sup> and Cu (II) concentrations: 1.3; 1.9; 2.5; 3.8; 5.1 and 6.4  $\mu$ g L<sup>-1</sup>.

## References

- 1 W. Song, L. Zhang, L. Shi, D.W. Li, Y. Li and Y.T. Long, Microchim. Acta, 2010, 169, 321-326.
- 2 S. Kucukkolbasi, Z.O. Erdoğan, J. Barek, M. Sahin and N. Kocak, Int. J. Electrochem. Sci , 2013, 8, 2164 2181.
- 3 N. Zhou, H. Chen, J. Li and L. Chen, *Microchim. Acta*, 2013, 180, 493–499.
- 4 Y. Fei, Z.Y. Lv, A.J. Wang, Y.H. Chen, J.R. Chen and J.J. Feng, Microchim. Acta, 2014, 181, 389–394.
- 5 A. Mandil, L. Idrissi and A. Amine, Microchim. Acta, 2010, 170, 299–305.
- 6 X.H. Gao, W.Z. Wei, L. Yang, T.J. Yin, Y. Wang, Anal. Lett., 2005, 38, 2327-2343.
- 7 F. El Aroui, S. Lahrich, A. Farahi, M. Achak, L. El Gaini, B. Manoun, M. Bakasse, A. Bouzidi, M.A. El Mhammedi, J. *Taiwan Inst. Chem. E.*, 2014, in press.
- 8. T.M. Arantes, A. Sardinha, M.R. Baldan, F.H. Cristovan, N.G. Ferreira, Talanta, 2014, 128, 132–140.
- 9. M. Rajabi, B. Mohammadi, A. Asghari, B. Barfi, M. Behzad, J. Ind. Eng. Chem., 2014, 20, 3737–3743.
- 10. M. Bagherzadeha, M. Pirmoradianb, F. Riahia, Electrochim. Acta, 115, 2014, 573-580.