

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI) for

Interfacing an heteropolytungstate complex and gelatin through a coacervation process: design of bionanocomposite films as novel electrocatalyst.

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Table 1. Main peaks in the FT-IR spectra of $[\text{BW}_{12}\text{O}_{40}]^{5-}$ -G hybrid and corresponding assignments.

Gelatin (cm^{-1}) ^f	Gelatin (this work) (cm^{-1})	$[\text{BW}_{12}\text{O}_{40}]^{5-}$ (cm^{-1}) ^g	$[\text{BW}_{12}\text{O}_{40}]^{5-}$ (this work) (cm^{-1})	$[\text{BW}_{12}\text{O}_{40}]^{5-}$ -G hybrid (this work) (cm^{-1})	Band assignments
1630	1648 (vs)			1646 (vs)	$\nu(\text{C}=\text{O})$, $\delta(\text{N}-\text{H})$
1541	1543 (s)			1536 (s)	$\delta(\text{N}-\text{H})$, $\nu(\text{C}-\text{N})$, $\nu(\text{C}-\text{C})$
1450	1452 (m)			1454 (m)	$\delta(\text{CH}_2)$
1410	1404 (sh)			1405 (sh)	$\nu(\text{COO})$
1334	1336 (w)			1336 (w)	$\delta(\text{CH}_2)$ wagging
12 35	1236 (w)			1238 (w)	$\nu(\text{C}-\text{N})$, $\delta(\text{N}-\text{H})$
1080	1078 (w)			1078 (vw)	Skeletal $\nu(\text{C}-\text{O})$
		960 (s)	957 (s)	956 (s)	$\nu_{\text{as}}(\text{W}-\text{O}_{\text{d}})$
		910 (s)	916 (s)	904(s)	$\nu_{\text{as}}(\text{B}-\text{O}_{\text{a}})$
		807 (vs)	804 (vs)	825(vs)	$\nu_{\text{as}}(\text{W}-\text{O}_{\text{c}}-\text{W})$

^f H. Staroszczyk, J. Pielichowska, K. Sztuka, J. Stangret, I. Kołodziejaska, *Food Chem.*, 2012, **130**, 335.

^g C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem.* 1983, **22**, 207-216.

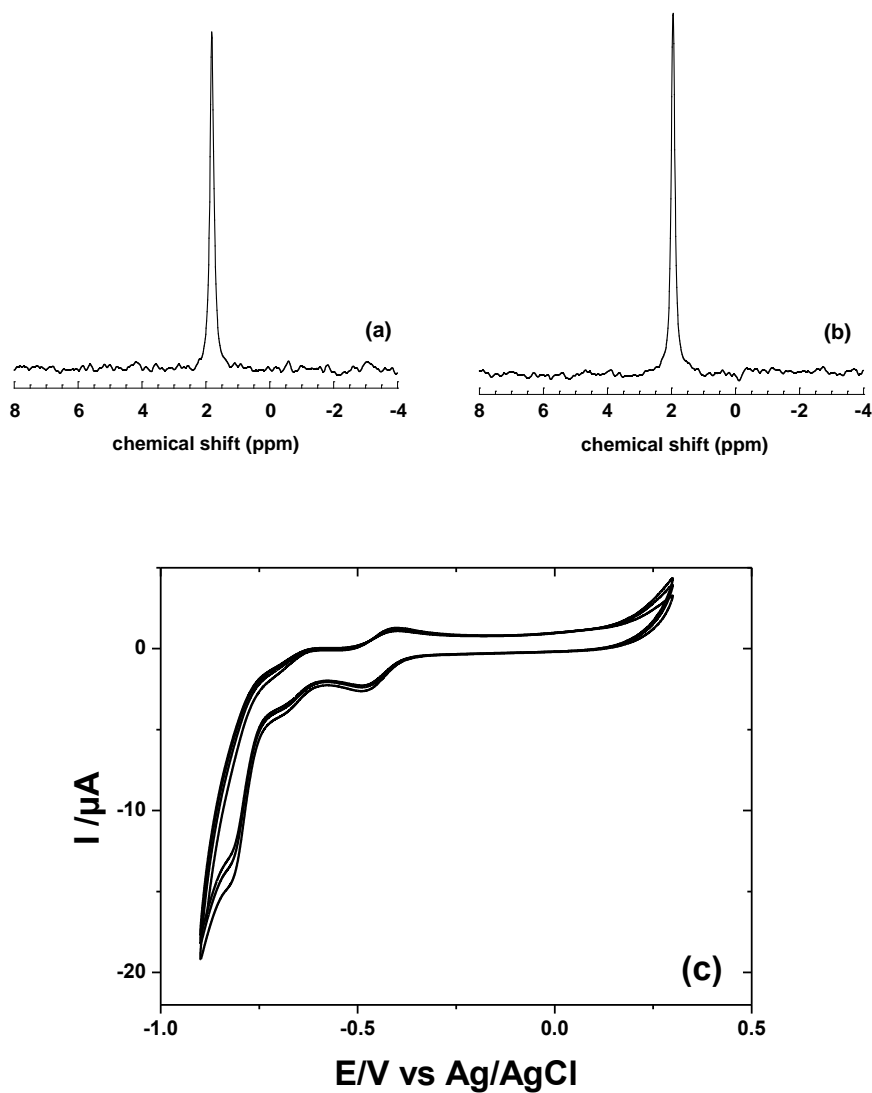


Figure S1. Characterization of $[\text{BW}_{12}\text{O}_{40}]^{5-}$ in aqueous solution ; (a)-(b) Solution ^{11}B NMR spectra of $[\text{BW}_{12}\text{O}_{40}]^{5-}$ ($c = 5 \cdot 10^{-4} \text{ M}$) at (a) pH 3 and (b) pH 4.7; (c) cyclic voltammogram of $[\text{BW}_{12}\text{O}_{40}]^{5-}$ ($c = 5 \cdot 10^{-4} \text{ mol.L}^{-1}$) in $\text{CHCl}_2\text{COOH}/\text{CHCl}_2\text{COONa}$ 1M-1M at pH 3, Electrolyte $0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution at pH 3. Scan rate: 100 mV s^{-1} .

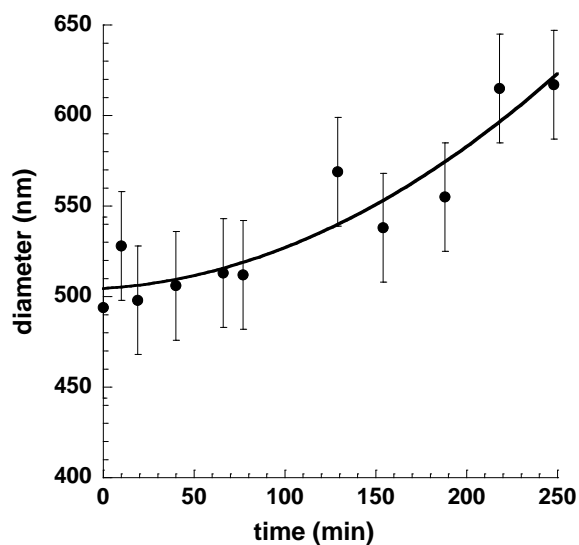


Figure S2. Evolution of colloids size (●) as measured by QELS upon ageing conditions without stirring ($T = 40^{\circ}\text{C}$, $\text{pH } 3$) for $[\text{G}] = 0.375 \text{ mM}$ and $[\text{BW}_{12}] = 0.23 \text{ mM}$. The continuous line corresponds to a second order polynomial fit and should be used as a guide for the eyes.

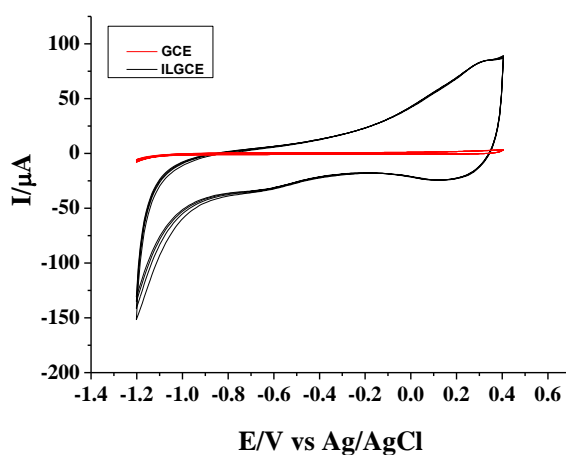


Figure S3. Cyclic voltammograms of GCE without ionic liquid and ILGCE (i. e. GCE modified with ionic liquid $[\text{bmim}][\text{PF}_6]$) in $0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution at $\text{pH } 3$. Scan rate: 100 mV s^{-1} .

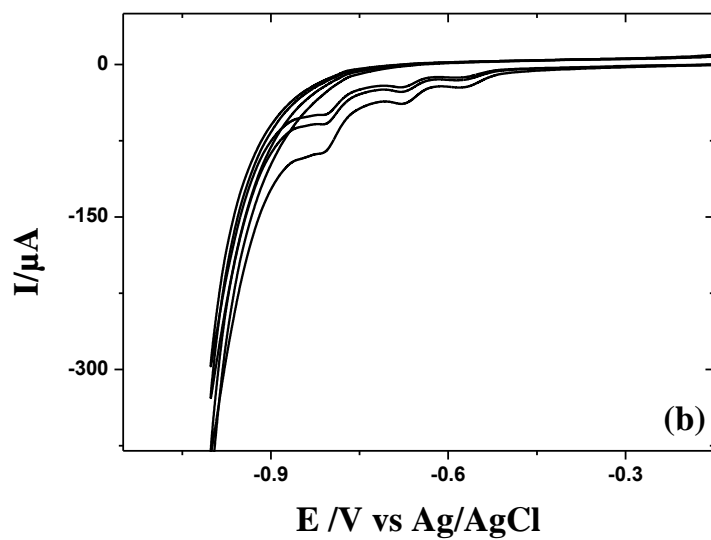
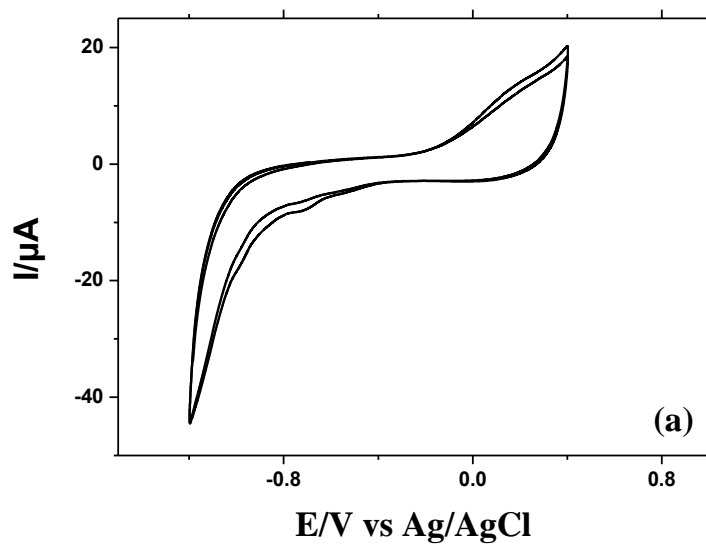


Figure S4. Cyclic voltammograms of (a) [BW₁₂]-ILGCE, (b) [BW₁₂]-G-ILGCE. Electrolyte 0.5 M Na₂SO₄ aqueous solution at pH 3. Scan rate: 10 mV s⁻¹.

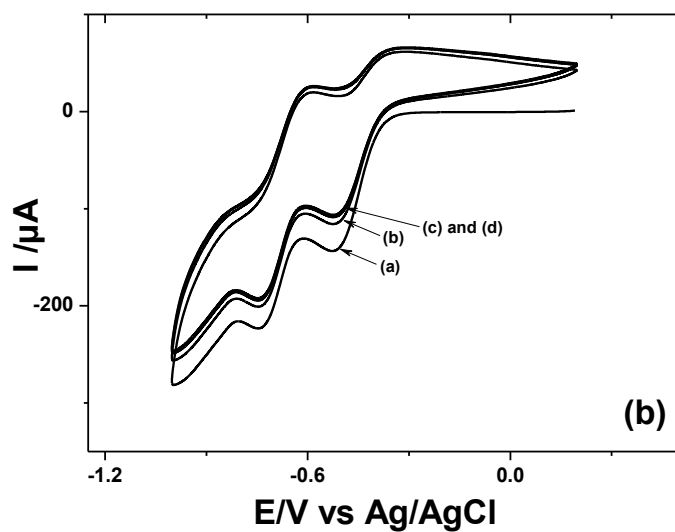
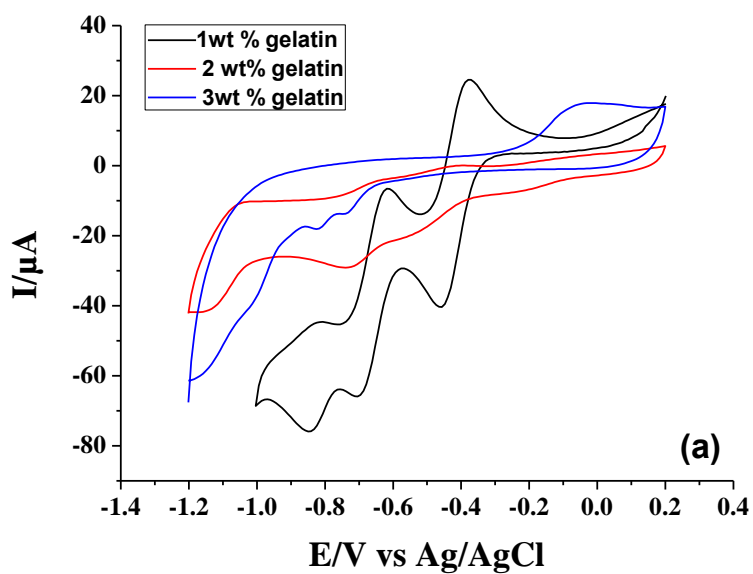


Figure S5. Cyclic voltammograms of (a) 2[BW₁₂]-G-ILGCE prepared with 1, 2 and 3 wt% of gelatin. Electrolyte 0.5 M Na₂SO₄ aqueous solution at pH 3. Scan rate: 10 mV s⁻¹. (b) 2[BW₁₂]-G-ILGCE in 0.5 M Na₂SO₄ aqueous solution at pH 3 at different cyclic numbers: (a) 1st, (b) 2nd, (c) 49th and (d) 50th cycles. Scan rate: 100 mV s⁻¹.

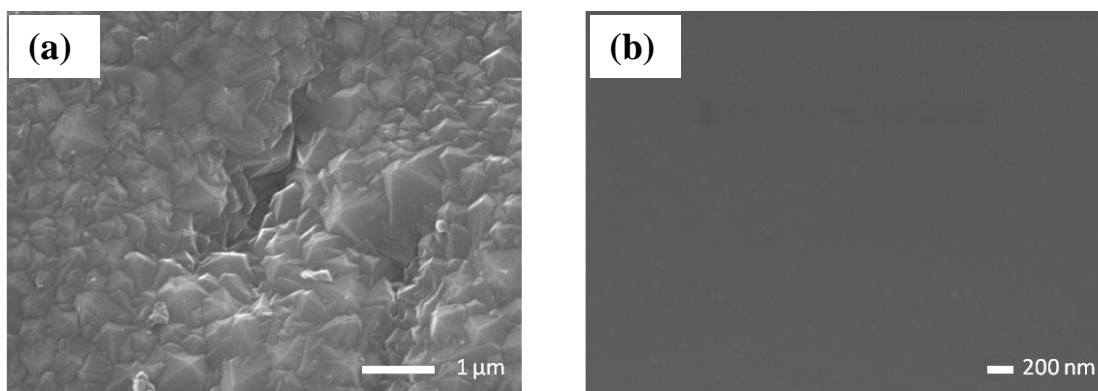


Figure S6. SEM images of (a) diamond wafer and (b) a gelatin film.

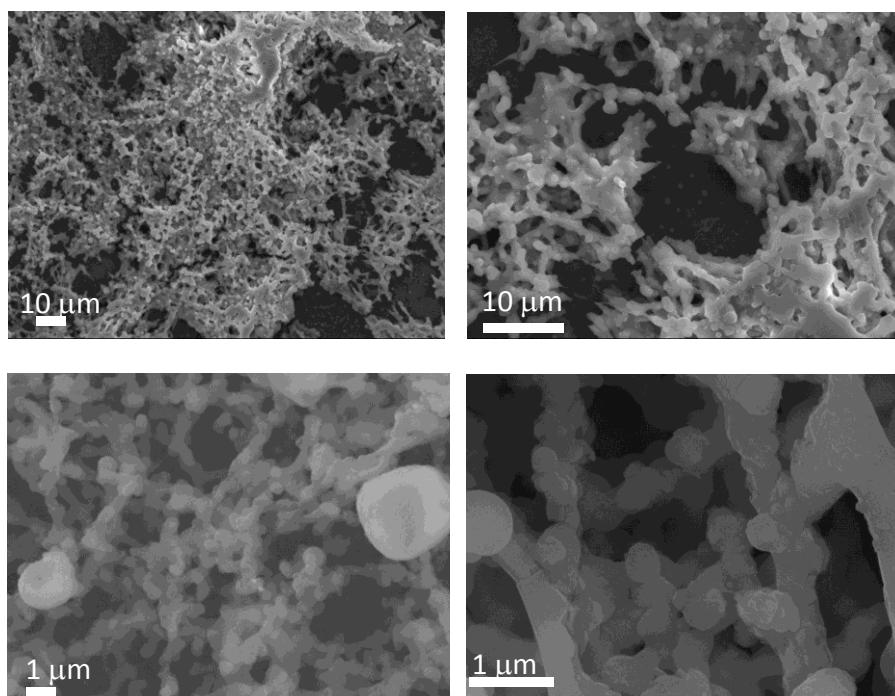


Figure S7. SEM images of 2[BW₁₂]-G-IL coatings prepared by deposition of 2 x 10 μL of a 0.5 mM [BW₁₂O₄₀]⁵⁻ solution and 10 μL of 1 wt% solution of gelatin.

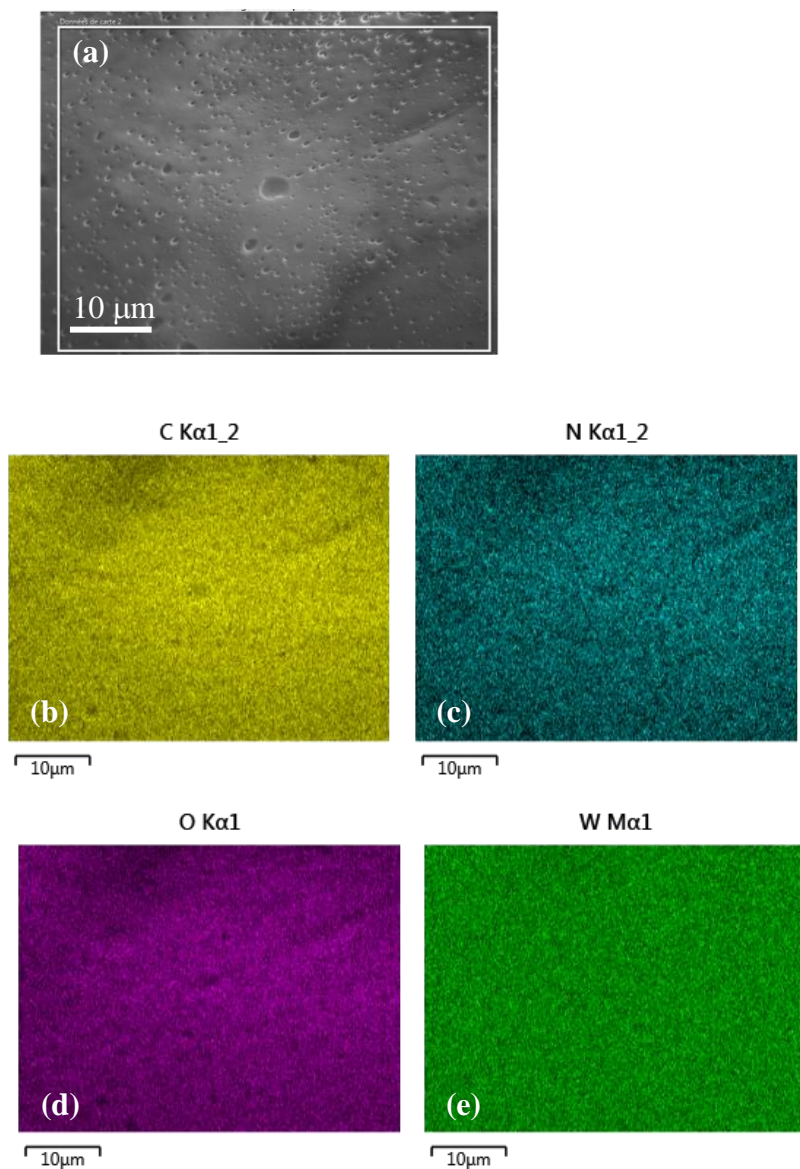


Figure S8. (a) SEM image of a 2[BW₁₂]-G-IL coatings prepared from the deposition of 2 x 20 μL of a 0.5 mM [BW₁₂O₄₀]⁵⁻ solution and 20 μL of 1 wt% solution of gelatin. (b-e) corresponding elemental mapping of carbon (b), nitrogen (c), oxygen (d) and tungsten (e) by EDX spectroscopy.