

Supplementary Data

Efficient Preparation of a Non-enzymatic Nanoassembly based on Cobalt substituted Polyoxometalates (Co-POM) and Polyethylene imine (PEI) capped Silver Nanoparticles (AgNPs) for the Electrochemical Sensing of Carbofuran

Amna Yaqub^{a*}, Syeda Rubina Gilani^a, Sehrish Bilal^b, Akhtar Hayat^b, Anila Asif^b, Saadat Anwar Siddique^b

- a. University of Engineering and Technology, Lahore, 54000, Pakistan,
- b. Interdisciplinary Research Center in Biomedical Materials (IRCBM), COMSATS University, Islamabad, Lahore Campus, Lahore 54000, Pakistan

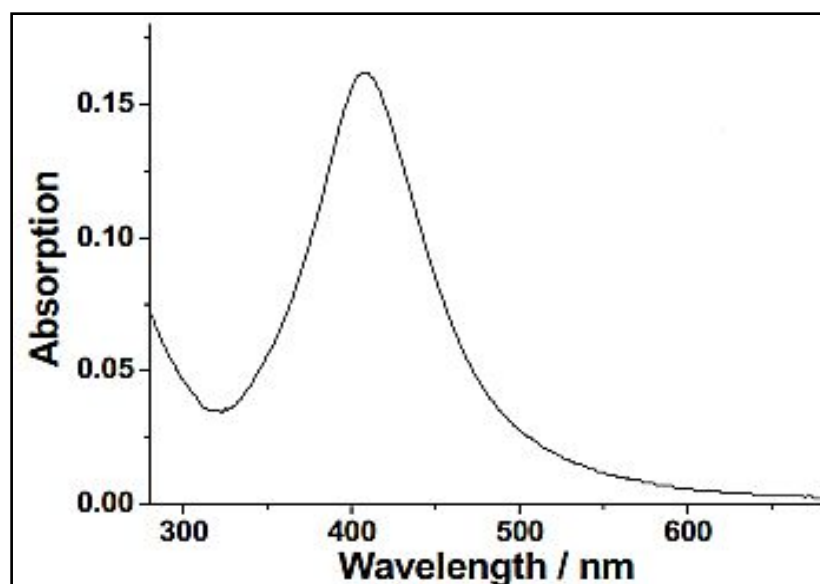


Figure S1: Typical UV-Visible spectrum of silver nanoparticles.

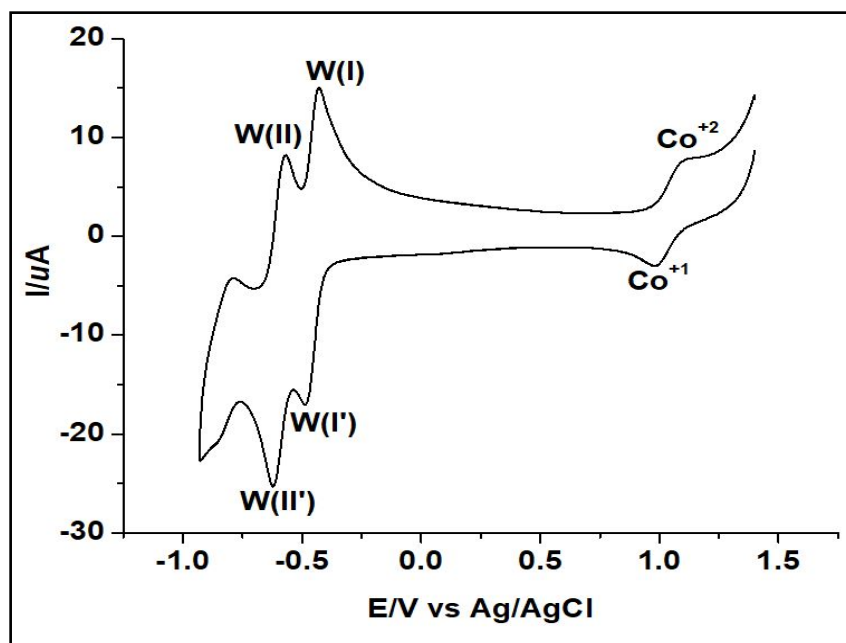


Figure S2: Solution phase cyclic voltammetry of cobalt substituted Dawson type polyoxometalate i.e. $\text{K}_8\text{P}_2\text{W}_{17}\text{O}_{61}(\text{Co}^{2+}\cdot\text{OH}_2)\cdot 16\text{H}_2\text{O}$ in pH 4.5 buffer vs. Ag/AgCl (reference), Scan rate was 100 mVs^{-1} at negative scan direction.

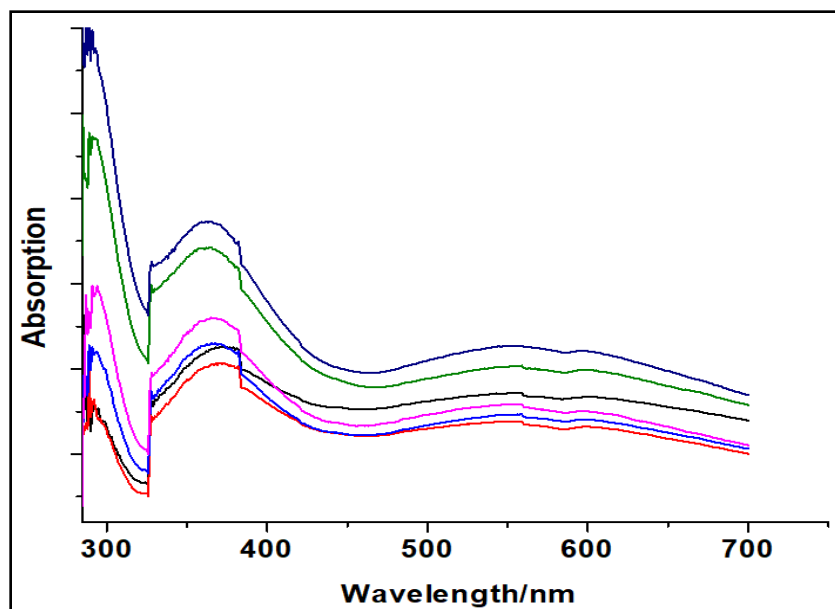


Figure S3: UV-Vis spectra of multilayer assembly based on PDDA/(POM/AgNPs) n composition having $n=6$ fabricated on ITO slide. The blank slide was used as a reference.

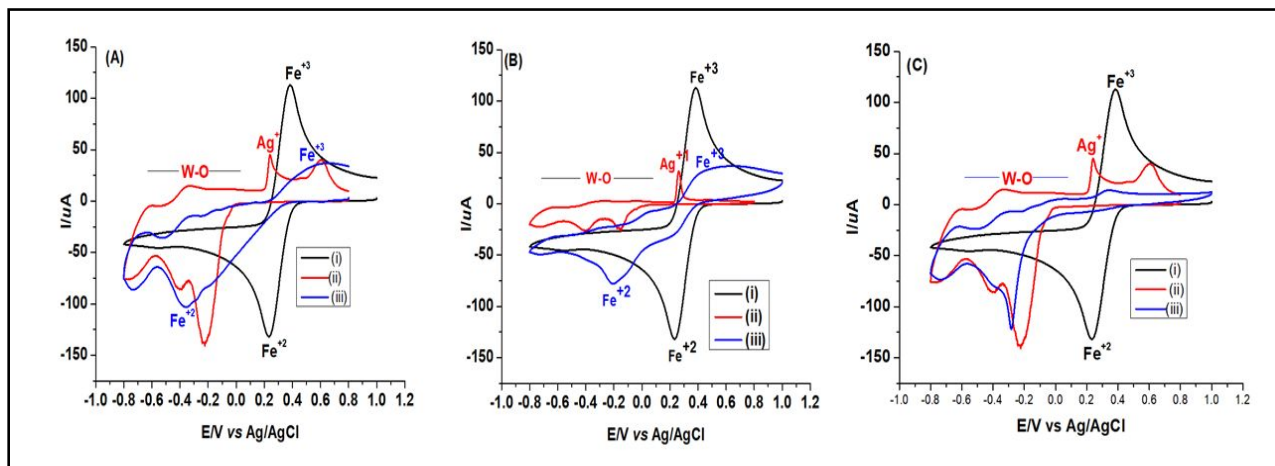


Figure S4: Permeability study: (A) Cyclic voltammograms recorded for (i) 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in buffer (0.1 M $\text{Na}_2\text{SO}_4/\text{pH } 2.0$) at clean GCE before any deposition, (ii) Co-POM/AgNP multilayer nanoassembly comprising of 4 bilayers with outermost POM layer (anionic) in the same buffer, (iii) Co-POM/AgNP hybrid film in 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in pH 2.0 buffer. (B) Overlay of cyclic voltammograms of (i) 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in buffer (0.1 M $\text{Na}_2\text{SO}_4/\text{pH } 2.0$) at clean GCE, (ii) Co-POM/AgNP multilayer film of 4 bilayers with outermost layer of cationic nanoparticles in the same buffer solution, (iii) Co-POM/AgNP hybrid film in of 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in pH 2.0 buffer. (C) Overlay of cyclic voltammograms of (i) 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in pH 2.0 buffer on clean GCE, (ii) Co-POM/AgNP hybrid film comprising 8 bilayers with outermost layer of anionic POM in pH 2.0 buffer, (iii) hybrid film in 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in pH 2.0 buffer (Scan rate was 100 mVs^{-1}).

Table S1: Comparison of average recovery values of carbamate pesticide in real samples with the previously reported methods.

| Method | Sample | Analysis time (min) | Concentrations (µg/kg) | Recoveries (%) | References |
|---|----------|---------------------|------------------------|----------------|------------|
| Micellar electrokinetic chromatography tandem mass spectrometry | Tomatoes | >120 | 10 | 81-99 | 1 |
| HPLC | Tomatoes | >180 | 10 | - | 2 |
| AChE/Con A/PDA-RGO-GNP/GCE | Tomatoes | 15-20 | 10 | 101 | 3 |
| HPLC-MS/MS | Tomatoes | 8 | - | Avg.63 | 4 |
| HPLC/DAD | Tomatoes | 10 | 30 | 84.5-88.1 | 5 |
| icELISA | Mango | >30 | 10 | 83.3 | 6 |
| UPLC-MS/MS | Mango | >10 | 10 | 84.7 | 6 |
| LC/DAD | Tomatoes | 10 | 60 | 65.8 | 7 |
| PDDA/Co-POM/AGNP/GCE | Tomatoes | <2 | 10 | 102 | This work |

References:

- 1: Moreno-Gonzalez, D., J. F. Huertas-Perez, A. M. Garcia-Campana, L. Gamiz-Gracia. Vortex-assisted surfactant-enhanced emulsification liquid–liquid microextraction for the determination of carbamates in juices by micellar electrokinetic chromatography tandem mass spectrometry. *Talanta* 2015, 139:174–80
- 2: Li, N., Chen J., Shi Y.P., Magnetic graphene solid-phase extraction for the determination of carbamate pesticides in tomatoes coupled with high performance liquid chromatography. *Talanta*, 2015, 141, 212–219.
- 3: Li Y., Li Y., Yu X., Sun Y., Electrochemical Determination of Carbofuran in Tomatoes by a Concanavalin A (Con A) Polydopamine (PDA)-Reduced Graphene Oxide (RGO)-Gold Nanoparticle (GNP) Glassy Carbon Electrode (GCE) with Immobilized Acetylcholinesterase (AChE), *Analytical Letters*, 2019, 14, 2283-2299.
- 4: Goto T., Ito Y, Oka H., Saito I., Matsumoto H., Sugiyama H., Ohkubo C., Nakazawa H., Nagase H., The high throughput analysis of N-methyl carbamate pesticides in wine and juice by electrospray ionization

liquid chromatography tandem massspectrometry with direct sample injection into a short column, Anal. Chim. Acta, 2005, 531, 79-86

5: Lin X.Y., Chen X.H., Huo X., Yu Z.G., Bi K.S., Li Q. Dispersive liquid–liquid microextraction coupled with high-performance liquid chromatography-diode array detection for the determination of *N*-methyl carbamate pesticides in vegetables, J. Sep. Sci., 2011, 34, 202-209.

6: Lan J., Wang M., Ding S., Fan Y, Diao X., Li Qing X., Zhao H., Simultaneous detection of carbofuran and 3-hydroxy-carbofuran in vegetables and fruits by broad-specific monoclonal antibody-based ELISA, Food Agric Immunol .2019, 30, 1085-1096.

7: Paíga P., Morais S., Correia M., Alves A., Matos C., Screening of Carbamates and Ureas in Fresh and Processed Tomato Samples using Microwave-Assisted Extraction and Liquid Chromatography, Anal. Lett., 2009, 42 265-283