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Graphene and Copper Nanoparticles based electrochemical sensors for the detection of Glyphosate in Water

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Glyphosate is the most widely used herbicide to control weeds in agriculture and various non-agricultural applications globally (Carretta, et al. *J. Chromatography.* A 1600, 2019), resulting in significant adverse impacts on the environment, especially contaminated soil and water, with potential effects on human health (Richmond, *AESS* 8, 2018). Such environmental threat recently triggered the development of enhanced and scalable glyphosate sensing technologies. Commercial sensors for the detection of glyphosate based on gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), quantum dots show a sensitivity ranging from 0.88 µM to few pM (Zúñiga, et al. *Water* 14, 15, 2022). In addition, the rigid nature of the current sensors limits the seamless integration with more sustainable substrates such as paper and textiles. Graphene is an excellent material for sensing applications (Fenech-Salerno, et al. *Nanoscale* 15, 7, 2023) (Schedin, et al. *Nat. Mater* 6, 9, 2007). Graphene offers a versatile platform for the detection of several analytes including glyphosate, owing to its high mobility, large surface area, high mechanical strength, and chemical stability. Graphene-based sensors offer a high sensitivity of the order of 0.30×10^{-12} M for glyphosate detection (Gonçalves, et al. *Mater. Today Commun.* 36, 2023). In addition, graphene inks enable a large range of printed, sustainable and flexible devices (Carey, et al. *Nat. Commun.* 8,1, 2017).

Here, we present the preparation of a glyphosate sensor based on graphene and Cu nanoparticles, deposited by a scalable spray-coating process on flexible substrate, such as polyimide (PI) and polyethylene terephthalate (PET). The graphene ink is prepared by liquid phase exfoliation, reaching a graphene concentration of ~ 0.7 mg/ml. The spray-coated graphene ink resulted in electrodes with a sheet resistance of ~ 240 Ω/□, subsequently spray coated with Cu nanoparticles synthesized using Pulsed Laser Ablation in Liquid (PLAL), with the concentration of 12.5 µg/ml, to form the Graphene/Cu nanoparticle (G:Cu) electrode.

The concentration of glyphosate was determined by Multiple Cyclic Voltammetry (CV) using the G:Cu electrode as the working electrode in a glass electrochemical cell loaded with a solution of glyphosate was prepared in Milli-Q water. The CV curve of G:Cu showed the presence of a redox reaction related to the oxidation states of copper ($Cu \rightarrow Cu^{2+}$), compared to a plain graphene electrode, thereby affirming the sensing efficacy of the glyphosate sensor. Our G:Cu sprayed sensor offers a flexible, sustainable, and scalable solution to detect glyphosate with excellent selectivity and sensitivity making it the perfect approach to address the need for accurate and efficient monitoring of glyphosate contamination in environmental and agricultural settings.