

Supplementary Information

Combining 3D printing and screen-printing in miniaturized, disposable sensors based on carbon paste electrodes

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CONTENTS

1. Study of reproducibility
2. Synthesis of Fe₃O₄ microspheres
3. pH optimization
4. Study of repeatability of Fe₃O₄-3D GPE
5. Study of volume

1. *Study of reproducibility*

Carbon pastes were prepared by hand-mixing appropriated amounts of carbon materials with mineral oil in a mortar during 15 min. Graphite paste was prepared using a proportion 70:30 (% weight) graphite: mineral oil. The carbon paste electrodes were prepared by filling the space for the working electrode on the fabricated device. The devices fabricated with graphite are referred to as Graphite/3D SPE. The suitability of the fabricated devices for electrochemical measurements was confirmed by cyclic voltammetry experiments. The electrochemical response of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe was investigated using Graphite/3D SPE. Figure S1A shows consecutive voltammograms with the same device but renewing the working electrode before every measurement. The voltammograms revealed well-defined reduction and oxidation peaks with a separation (ΔE_p) of ~ 172 mV. The relative standard deviation (RSD) for the oxidation peak current was 5.9%, thus indicating good reproducibility of the device. The 3D printed device also exhibits high fabrication repeatability, with an RSD of 4.0% calculated for three different Graphite/3DSP cells (Figure S1B).

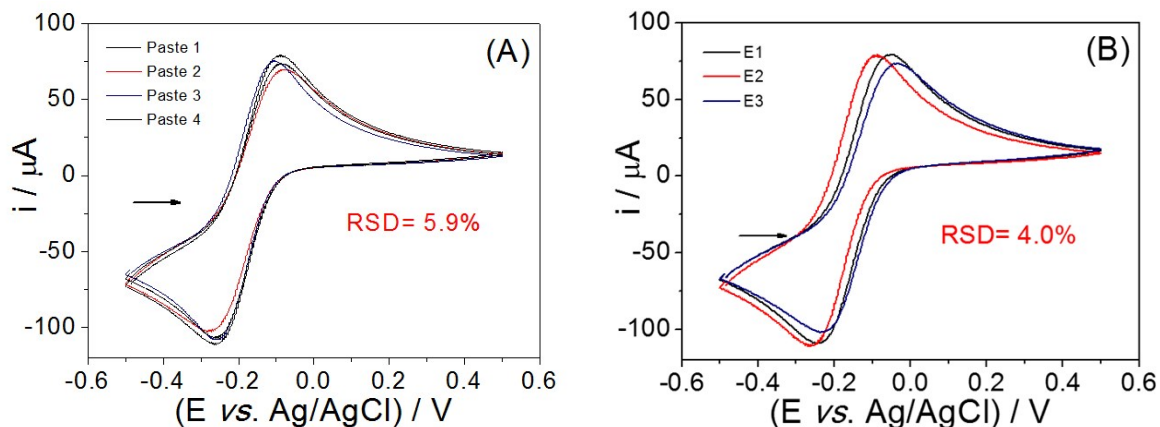


Figure S1. Cyclic voltammograms for solutions containing $5.0 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3\text{Fe}(\text{CN})_6$ in $\text{KCl } 0.1 \text{ mol L}^{-1}$ using graphite paste electrodes prepared with the same fabricated devices (A) and with three different devices (B). $\nu = 100 \text{ mV s}^{-1}$.

2. Synthesis of Fe_3O_4 microspheres

The microspheres were prepared using the solvothermal method illustrated in Figure S2. Briefly, 2.70 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 mL ethylene glycol (EG) to form a clear solution, followed by adding a 7.20 mg sodium acetate. The solution was left under vigorous stirring for 1 h to form a homogeneous yellow solution. It was then transferred to a stainless-steel autoclave, heated at $200 \text{ }^\circ\text{C}$ for 8 h and cooled to room temperature. The resultant microspheres were washed several times with deionized water, ethanol and collected by centrifugation and dried in a vacuum oven overnight at $80 \text{ }^\circ\text{C}$. [1]

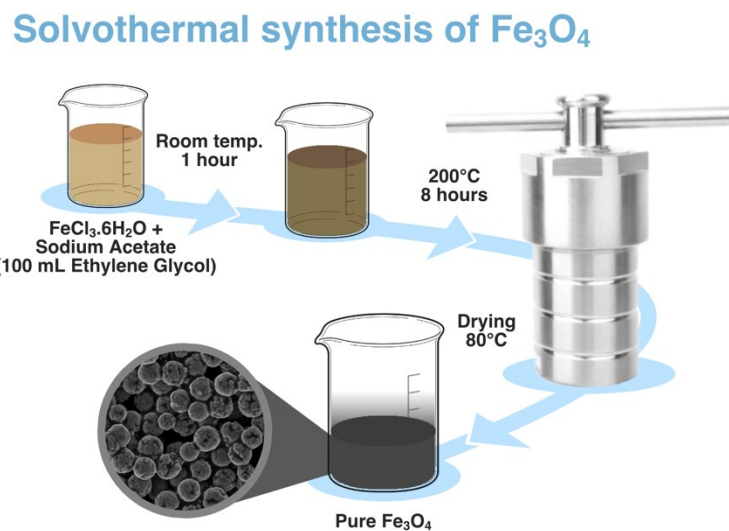


Figure S2. Schematic synthesis of Fe₃O₄ *microspheres*

3. *pH optimization*

An optimized performance in terms of higher peak currents and sharper peak definition was obtained at pH 6, as indicated by the SW voltammograms in Figure S3. The measurements were carried out in the presence of 4.5×10^{-5} mol L⁻¹ DOP (A), 5.0×10^{-6} mol L⁻¹ NIM (B) and 1.0×10^{-5} mol L⁻¹ UA (C) in 0.1 mol L⁻¹ phosphate buffer solutions.

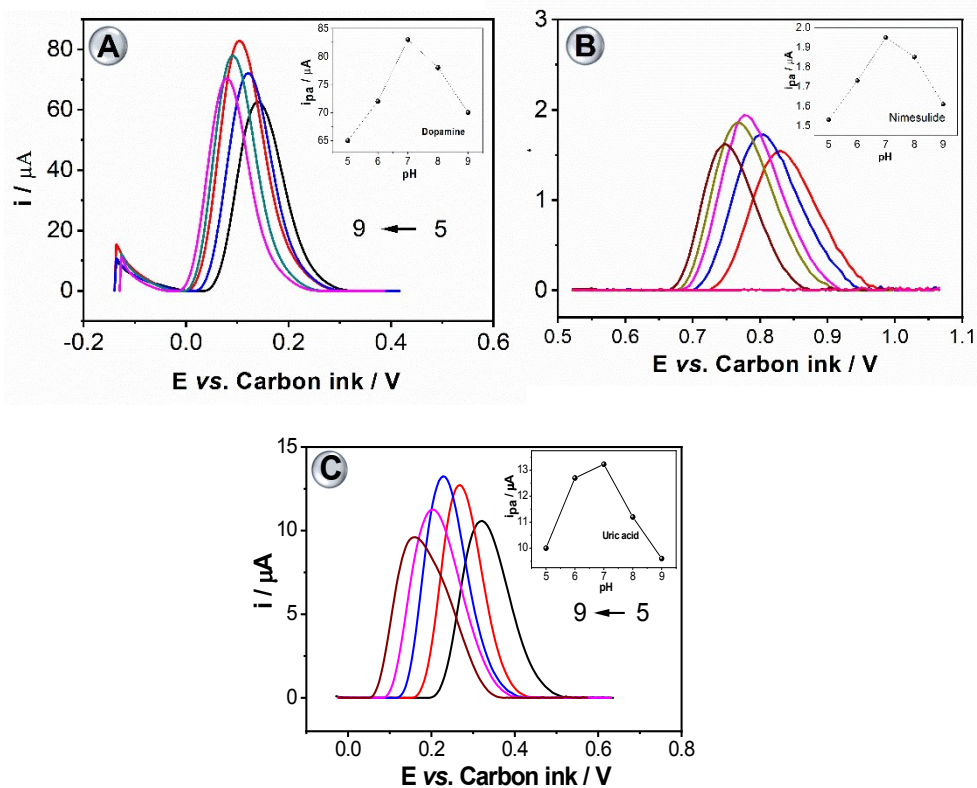


Figure S3. SW voltammograms for (A) $4.5 \times 10^{-5} \text{ mol L}^{-1}$ DOP, (B) $5.0 \times 10^{-6} \text{ mol L}^{-1}$ NIM and $1.0 \times 10^{-5} \text{ mol L}^{-1}$ UA (C) in 0.1 mol L^{-1} phosphate buffer solution (pH from 5 to 9). Inset: I_p vs pH. Conditions: $f = 15 \text{ Hz}$, $A = 50 \text{ mV}$ and $\Delta E = 5 \text{ mV}$, DOP: NIM: and UA: $f = 15 \text{ Hz}$, $A = 50 \text{ mV}$ and $\Delta E = 5 \text{ mV}$.

The results for different amounts of nimesulide and from the repeatability study are shown in Figures S4 and S5, respectively.

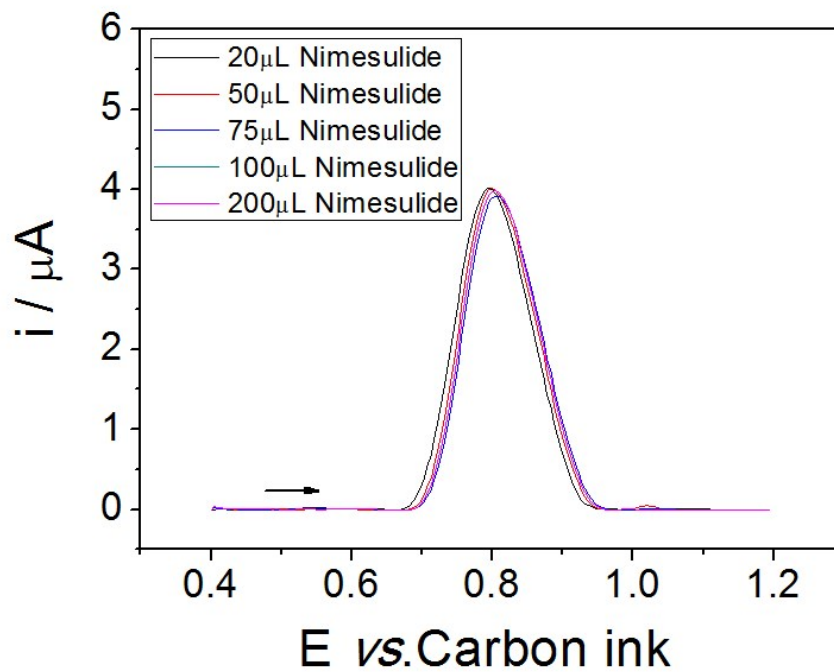


Figure S4. Amount of solution used in the experiments with the proposed sensor

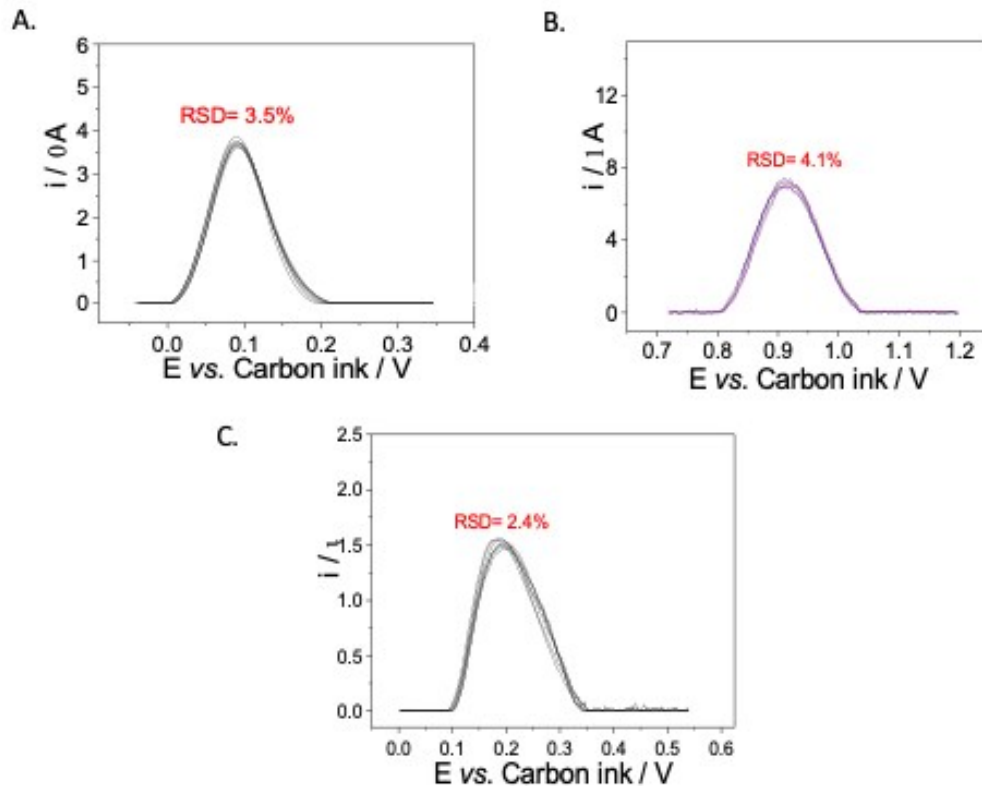


Figure S5: Study of repeatability of the Fe₃O₄-GR/SPE sensor in presence of **A.** 2.0×10^{-6} mol L⁻¹ dopamine. Conditions: $f = 15$ Hz, $A = 50$ mV and $\Delta E = 5$ mV **B.** Conditions: $f = 20$ Hz, $A = 75$ mV and $\Delta E = 5$ mV [Nimesulide] = 2.0×10^{-5} mol L⁻¹ **C.** Conditions: $f = 15$ Hz, $A = 50$ mV and $\Delta E = 5$ mV, [Uric acid] = 1.0×10^{-6} mol L⁻¹

Reference

- [1] J. Huang, Y. Li, X. Jia, H. Song, Preparation and tribological properties of core-shell Fe₃O₄@C microspheres, *Tribol. Int.* 129 (2019) 427–435.
 doi:10.1016/j.triboint.2018.08.036.