**Supporting information**

# *In-situ* biomimetic mineralization of paper microfluidic device as luminescent sensor for nitrite determination

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**SI1. Nitrite quantification in drinking water by Griess-Saltzman method**

Nitrite concentration in tap water from Granada and Zaragoza was measured by a gold standard methodology, Griess-Saltzman method, through the protocol previously described elsewhere.[1,2] Two solutions, (A) 1mg/mL of an aqueous solution of N-(1-naphthyl)ethylenediamine dichlorohydrate and (B) 10 mg/mL of an aqueous solution containing sulfanilamide and 5mL of phosphoric acid were mixed in a 1:1 ratio to obtain Griess' reagent. Different standard nitrite solutions (10 mL) of known concentrations (0.005-0.6 ppm) were prepared to obtain a calibration line. 125 µL of Griess' reagent was added to 2.5 mL of each nitrite solution and the reaction was allowed to proceed for 30 min. A diazo reaction occurs in which nitrite ions react with sulphanilamide to form a diazonium salt, which in turn reacts with N-(1-naphthyl)ethylenediamine dichlorohydrate to form a pink azo compound. After the reaction, the absorbance was measured (543 nm) and a calibration curve was obtained (Fig. SI1).
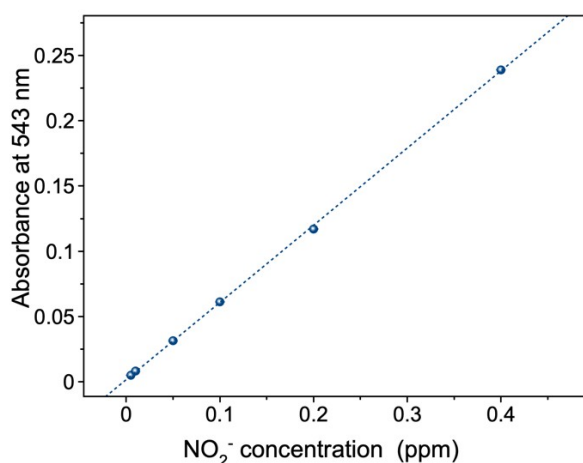


**Figure SI1.** Calibration curve of nitrite concentration in water through Griess-Saltzman method. Dots display the absorbance at 543 nm after Griess reaction and the dotted line represents the best fits of the experimental data according to the equation: $Abs = 0.592$ $[NO_2^-] + 0.0016$ $R^2 = 0.999$.
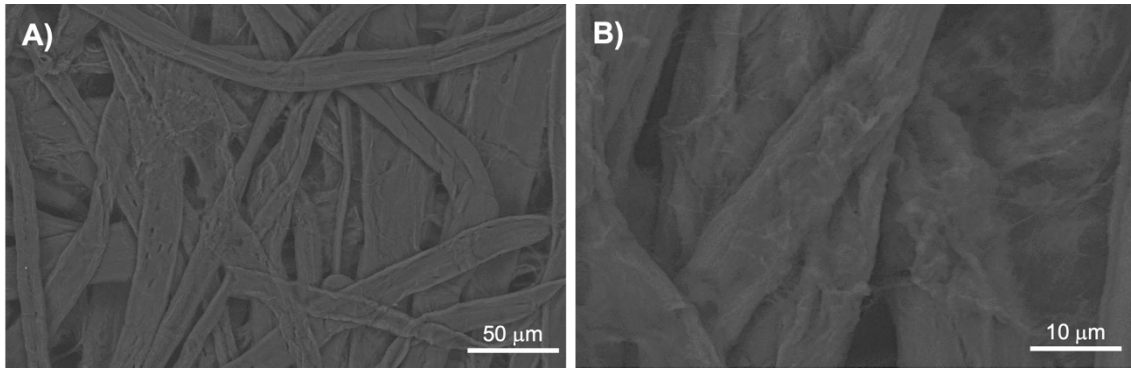
**Figure SI2.** Scanning electron microscopy images in backscattering mode (SEM-BSE) of non-mineralized cellulose fibres of the µPAD (control).
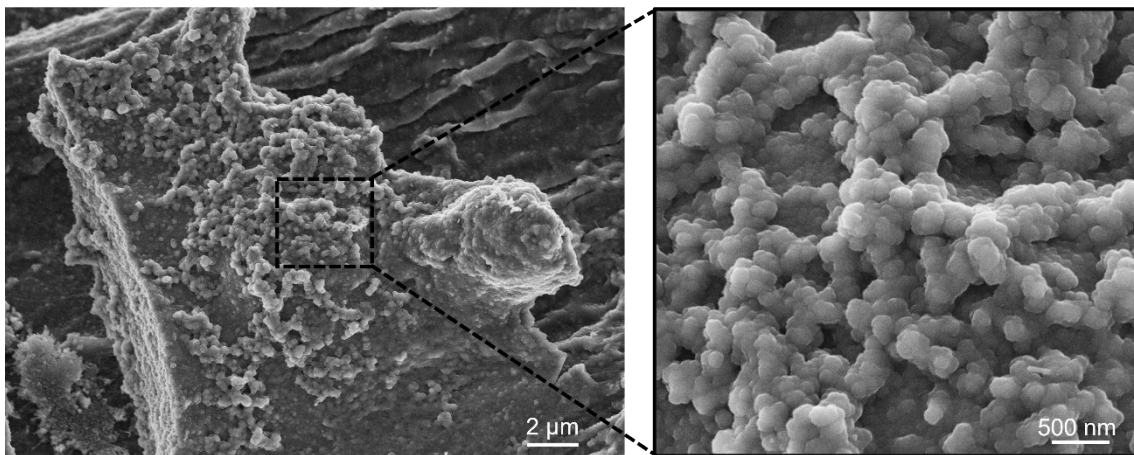


**Figure SI3.** SEM images of Tb-ACP nanoparticles precipitated in cellulose fibre via optimized multiple-steps in-situ mineralization.
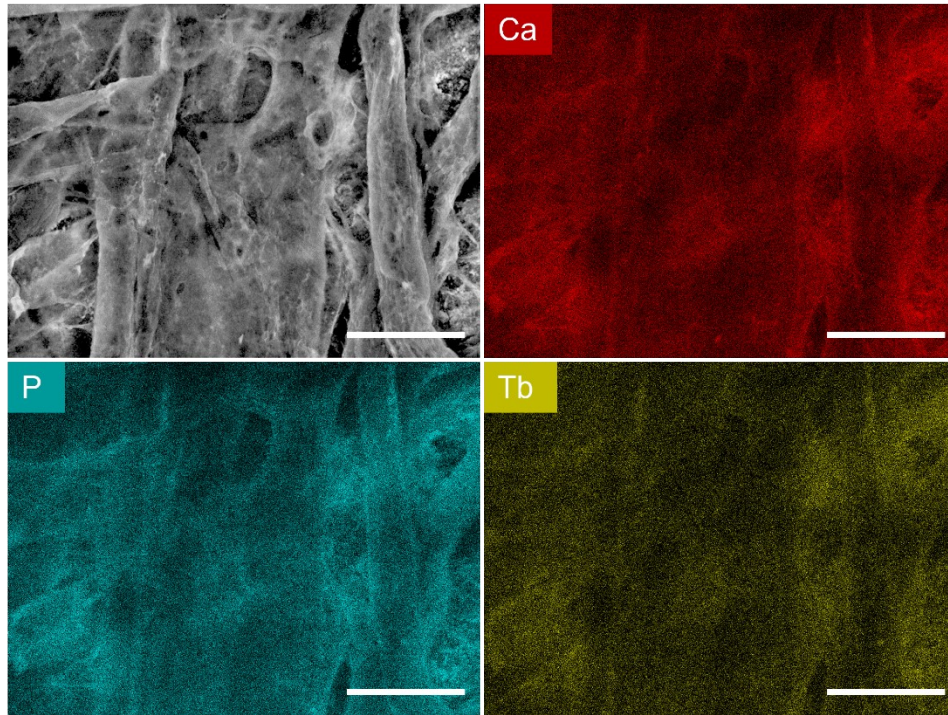
**Figure SI4.** SEM image and Energy dispersive X-ray spectroscopy (EDS) elemental maps of an area of the mineralized cellulose disk of the µPAD showing the spatial distribution Ca (red), P (blue) and Tb (yellow) of the mineral phase. Scale bar= 25 µm.
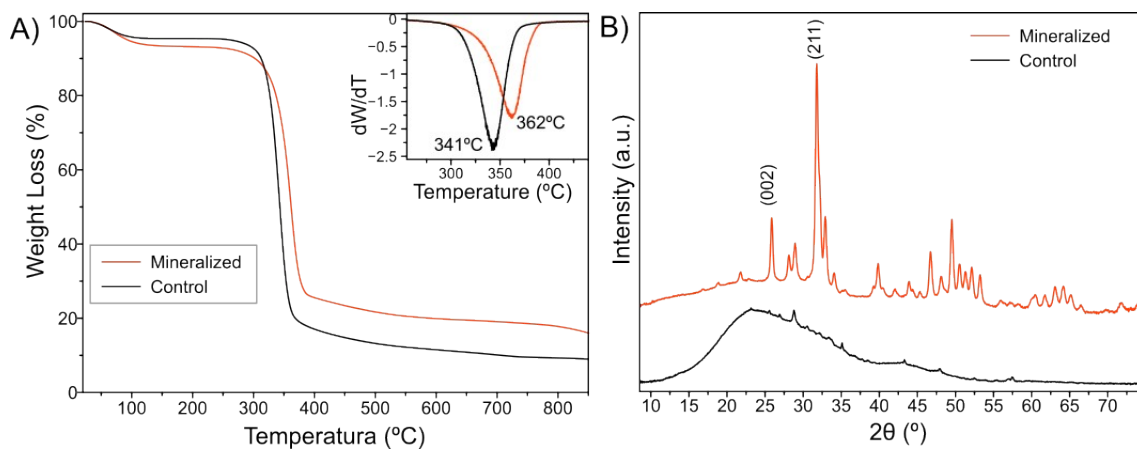


**Figure SI5.** (A) Thermogravimetric analysis of mineralized and control cellulose samples and (B) XRD patterns of the powder obtained after TGA analysis of ash content. In the case of mineralized cellulose, the XRD pattern is assigned to hydroxyapatite (HA, ASTM card file No: 09-432).
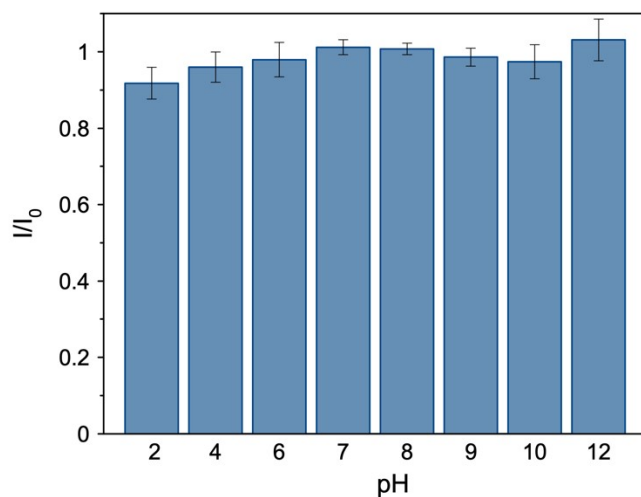
**Figure SI6**. Normalised luminescence intensity of mineralized μPAD as a function of the pH value. $I_0$ and I refer to the intensity of the emission peak at 546 nm measured at neutral pH and at specific pH, respectively.
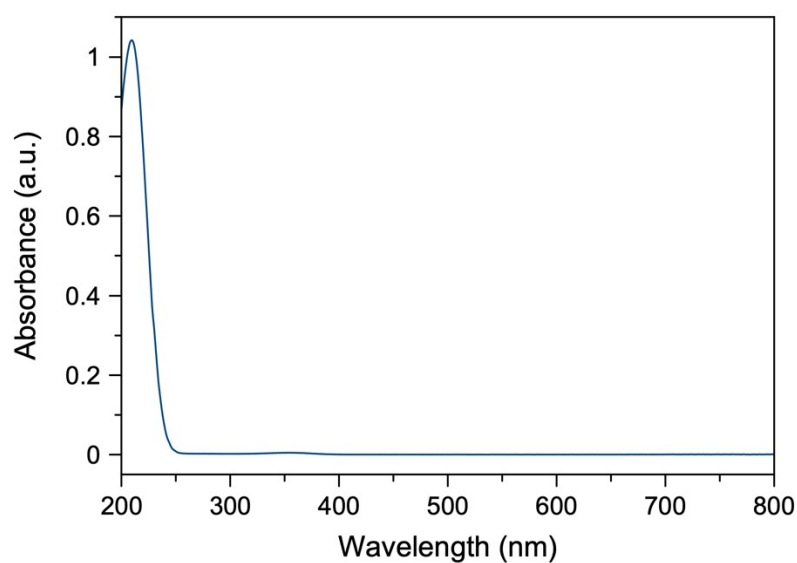


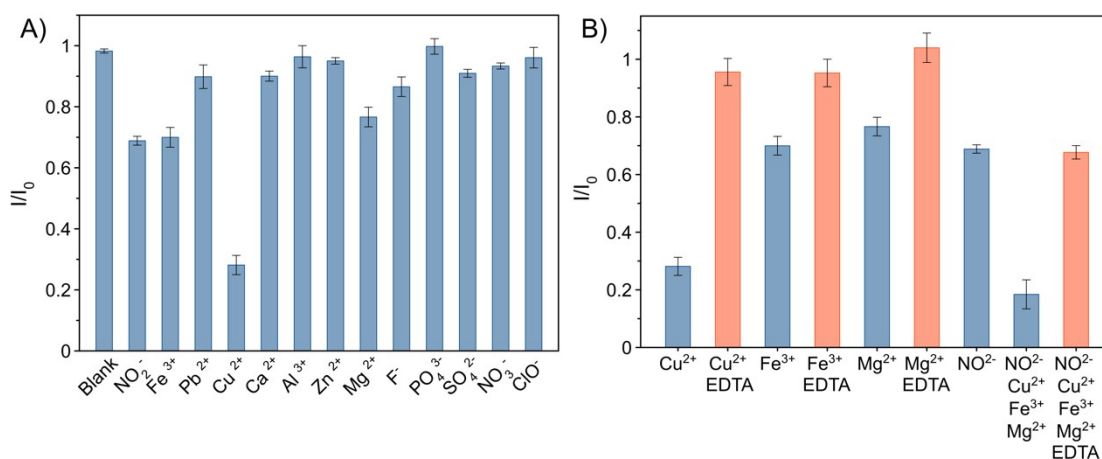**Figure SI7:** UV-Vis spectrum of sodium nitrite solution (200 μM).

**Figure SI8.** A) Normalised luminescence emission intensities of designed μPAD in the presence of $NO_2^-$, $Fe^{3+}$, $Pb^{2+}$, $Cu^{2+}$, $Ca^{2+}$, $Al^{3+}$, $Zn^{2+}$, $Mg^{2+}$, $F^-$, $PO_4^{3-}$, $SO_4^{2-}$, $NO_3^-$ and $ClO^-$ ions at a final concentration of 200 μM. A blank experiment in the absence of interfering species was also measured (Blank, $I_0$). B) Normalised luminescence emission intensities of designed μPAD in the presence of $Cu^{2+}$ (200 μM), $Fe^{3+}$ (200 μM)., $Mg^{2+}$ (200 μM), $NO^{2-}$ (200 μM), and all the ions together in the absence and presence of EDTA solution in the microfluidic channel.

**Table SI1.** Atomic concentration of naked cellulose and mineralized cellulose calculated by XPS spectrum.

| | C1s | O1s | P2p | Ca2p | Tb3d |
|---|---|---|---|---|---|
| **Control** | 60.00 | 39.97 | | | |
| **Mineralized** | 44.21 | 43.31 | 6.06 | 5.57 | 0.86 |

**Table SI2**. Recovery study for nitrite in tap water spiked with 200 µM, 65 µM (*i.e.,* the maximum contaminant level of nitrite ions in drinking water established by the World Health Organization)[3,4] and 10 µM (*i.e.,* LOD of designed µPAD) of nitrite standard.

| Sample | Nitrite added, µM | Nitrite found, µM | Recovery (%) n=3 |
|---|---|---|---|
| | 200 | 209.07 ± 1.48 | 104.54 |
| Tap water, Zaragoza | 65 | 65.64 ± 0.41 | 100.98 |
| | 10 | 9.55 ± 3.26 | 95.56 |
| | 200 | 199.62 ± 1.35 | 99.80 |
| Tap water, Granada | 65 | 68.49 ± 1.00 | 105.37 |
| | 10 | 9.52 ± 0.33 | 95.22 |

**References**

1    W. Fresenius, K. E. Quentin, W. Schneider and E. Lopez-Ebri, Water Analysis: A Practical Guide to Physico-Chemical, Chemical, and Microbiological Water Examination and Quality Assurance, 1988.

2    K. M. Miranda, M. G. Espey and D. A. Wink, A rapid, simple spectrophotometric method for simultaneous detection of nitrate and nitrite, *Nitric oxide*, 2001, **5**, 62–71.

3    J. A. Cotruvo, 2017 WHO guidelines for drinking water quality: first addendum to the fourth edition, *Journal-American Water Works Association*, 2017, **109**, 44–51.

4    N. S. Bryan, D. D. Alexander, J. R. Coughlin, A. L. Milkowski and P. Boffetta, Ingested nitrate and nitrite and stomach cancer risk: an updated review, *Food and Chemical Toxicology*, 2012, **50**, 3646–3665.