Fully inkjet-printed poly(N-isopropylacrylamide)/graphene electrodes for electroanalytical sensing with pH switchable selectivity

- Supporting Information -

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Table of Contents

SI-1: Circular reduced working electrode area

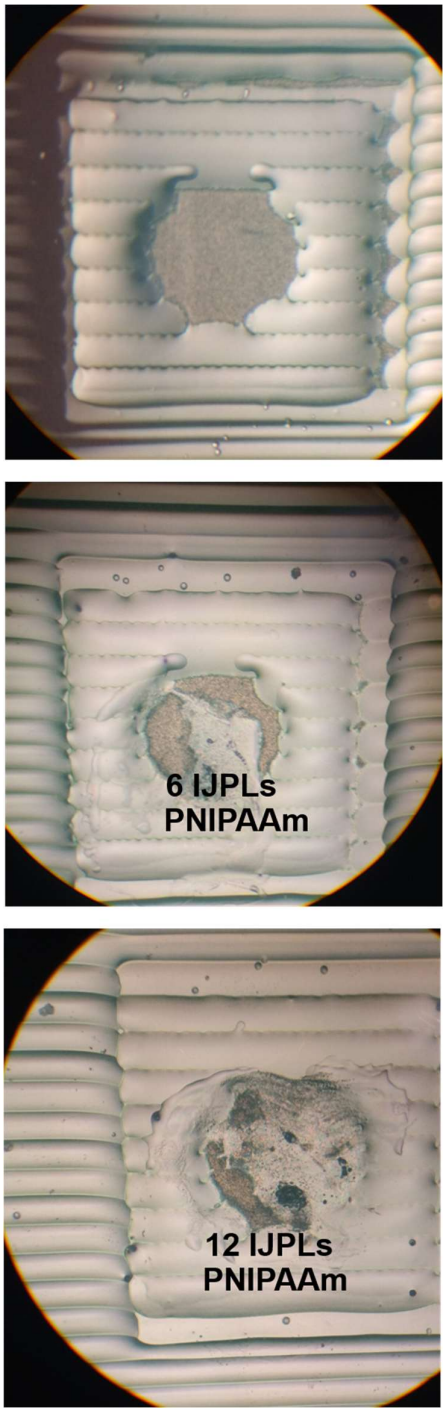

Fig. S1. Optical micrographs of PNIPAAm IJP on reduced circular working electrode areas. Upper panel shows the bare graphene electrode while the other two frames show 6 and 12 inkjet printed hydrogel layers, respectively. Homogeneous and complete graphene electrode coverage was not achieved by this approach.

SI-2: Thickness estimation of the PNIPAAm layer

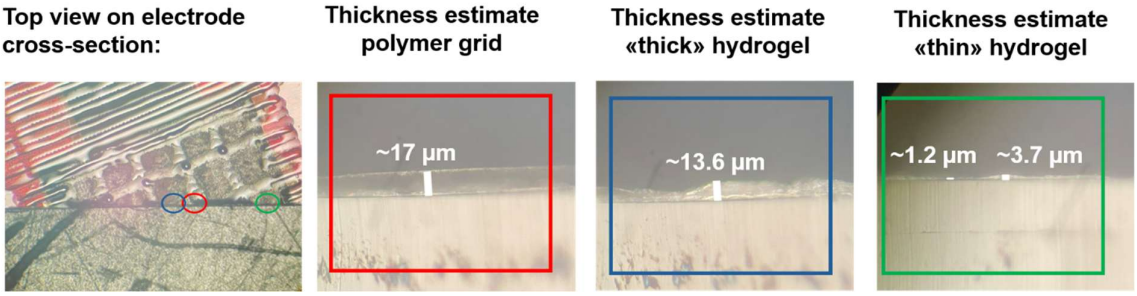

Fig. S2. Optical micrographs (top view and cross-sectional views) for the estimation of the thickness of the PNIPAAm layer. Colour codes indicate the locations along the cross-sectional line of an IJP PNIPAAm/G electrode (Grid-3, 6 IJPL).

SI-3: PNIPAAm/graphene electrode stabilization after immersion into solution

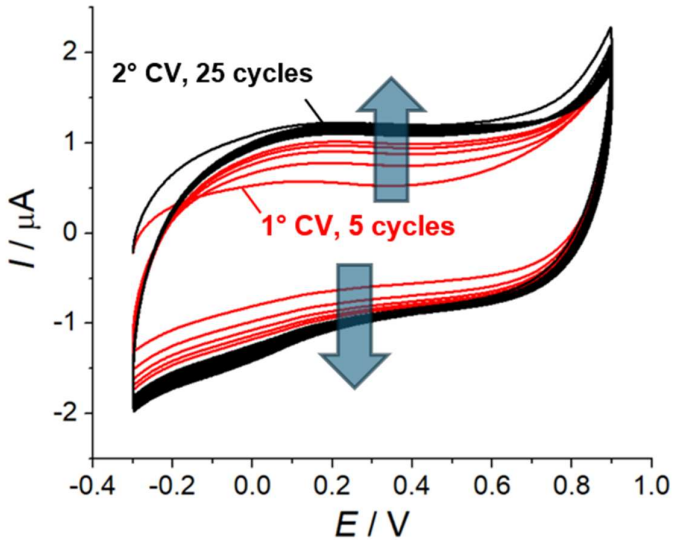

Fig. S3. CV in 0.1 M phosphate buffer (pH 7.4) using a PNIPAAm/graphene electrode (Grid-3, 6 IJPLs), showing the data of two consecutive CVs, the first with 5 cycles (red curve) and the second with 25 cycles (black). Scan rate 100 mV/s.

A dried hydrogel-coated electrode was immersed into the solution and the first CV experiment immediately started. From these results it is assumed that the hydrogel swelling reaches steady-state after a couple of minutes.

SI-4: Stability test of the PNIPAAm/graphene electrode during CV cycling

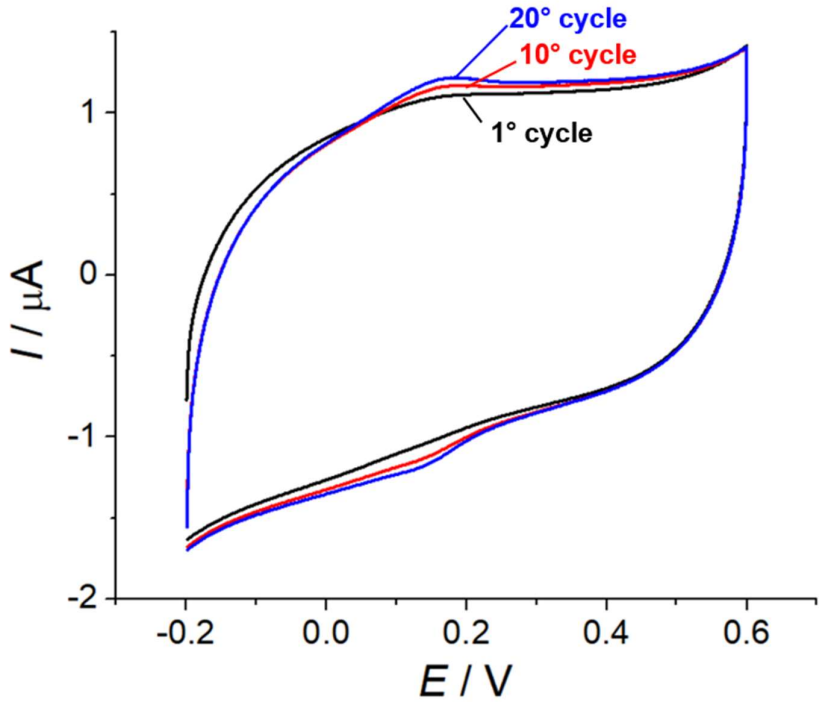

Fig. S4. CV in 1 mM $[Fe(CN)_6]^{3-}$ and 0.1 M KNO_3 using a PNIPAAm/graphene electrode (Grid-3, 6 IJPLs), showing the first (black curve), tenth (red) and twentieth (blue) CV cycle. Scan rate 100 mV/s.

These results suggest that even when the hydrogel is stably swollen, over time, the blocking effect slightly reduces for a hydrated PNIPAAm/graphene electrode.

SI-5: Thermo-response of the bulk PNIPAAm hydrogel

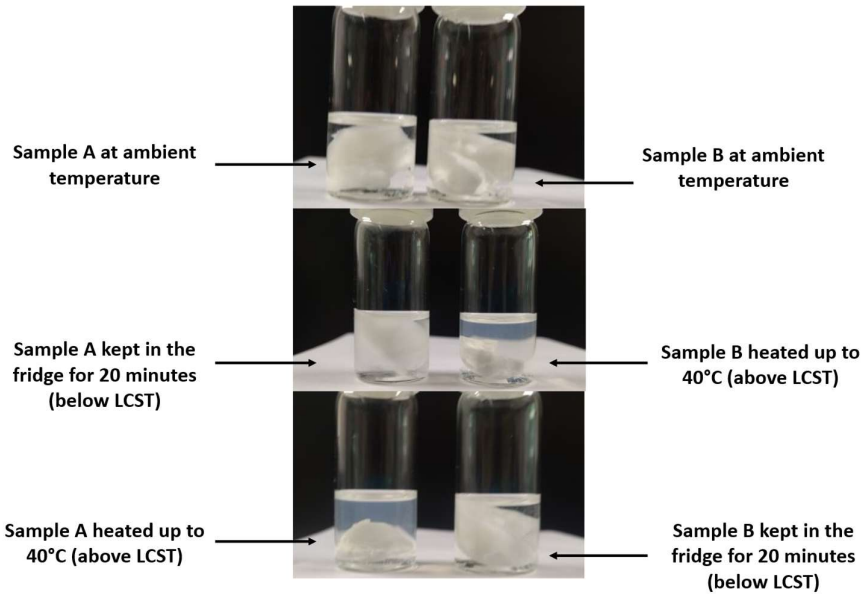

Fig. S5. Bulk PNIPAAm analysis at different temperatures. Two identically prepared bulk PNIPAAm pieces in water, denominated Samples A and B, at ambient temperature (upper frame). Sample A was then kept in a fridge for 20 minutes while Sample B was heated to 40 °C (middle frame). Then Sample A was heated to 40 °C and Sample B was kept in the fridge for 20 minutes.

The bulk PNIPAAm pieces, prepared identically to the inkjet-printed layers, demonstrated clearly the well known and reversible thermo-responsive behaviour, *i.e.*, shrinking of the PNIPAAm above the LCST (with turbid solution appearance) and swelling in a fridge (with clear, turbid-free water phase). Hence, the synthesized PNIPAAm material behaved in bulk form as reported in the literature and expected.

SI-6: Dopamine detection in presence of ascorbate

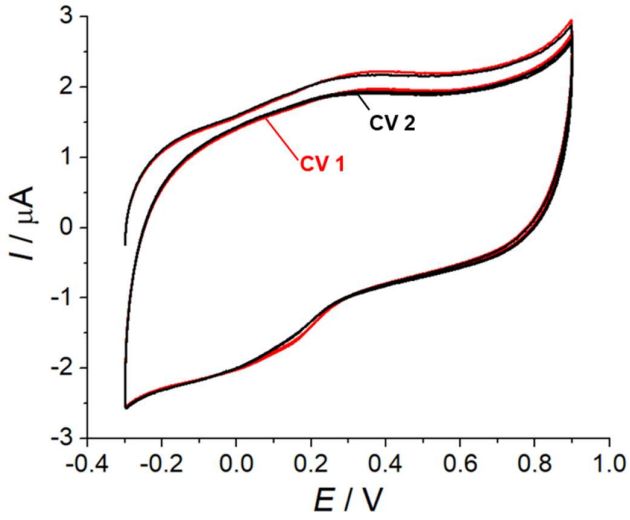

Fig. S6-1. CVs using one hydrated PNIPAAm/G electrode in 5 mM ascorbic acid in PB solution with pH 7.4. Scan rate 100 mV/s. CVs 1 and 2 were recorded separately after removal of the electrode from the solution, rinsing with water and reconditioning in PB solution.

After hydrogel swelling reached steady-state, the sensor response was stable.

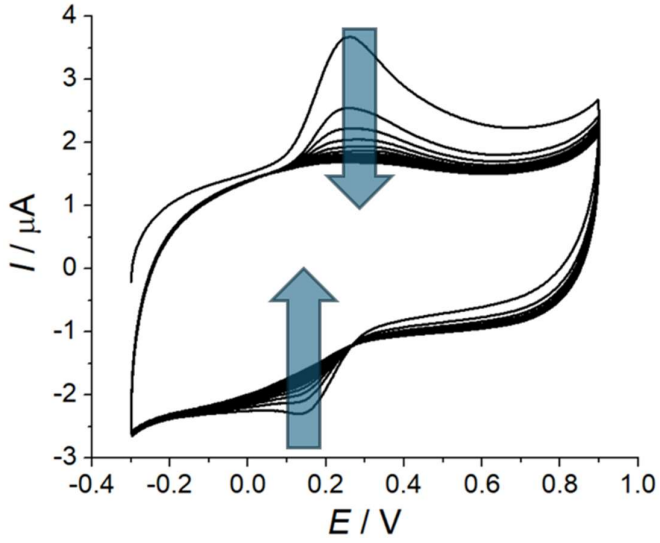

Fig. S6-2. Reconditioning of a PNIPAAm/G electrode after usage in a solution containing a detectable redox species, such as 1 mM dopamine, in PB solution with pH 7.4. 15 CV cycles. Scan rate 100 mV/s.

The hydrogel can still contain attracted redox species from previous measurements, even after rinsing with DI water. During immersion of the "contaminated" PNIPAAm/G electrode in PB solution the redox species diffuse away from the electrode. Therefore, the electrodes can be reused. As the hydrogel absorbs and retains redox species, conditioning of the electrodes in analyte-free electrolytes is required.

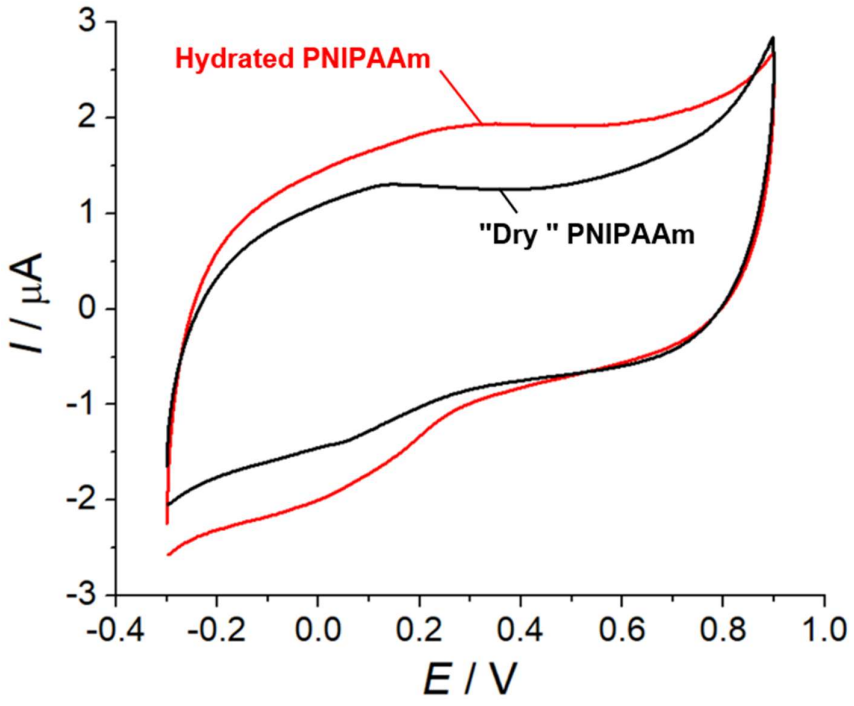

Fig. S6-3. CVs using a dry (*i.e.*, just immersed) and hydrated (*i.e.*, stably swollen) PNIPAAm/G electrode in 5 mM ascorbic acid in PB solution with pH 7.4. Scan rate 100 mV/s.

A just immersed, yet poorly swollen hydrogel blocks more efficiently the ascorbate ion.

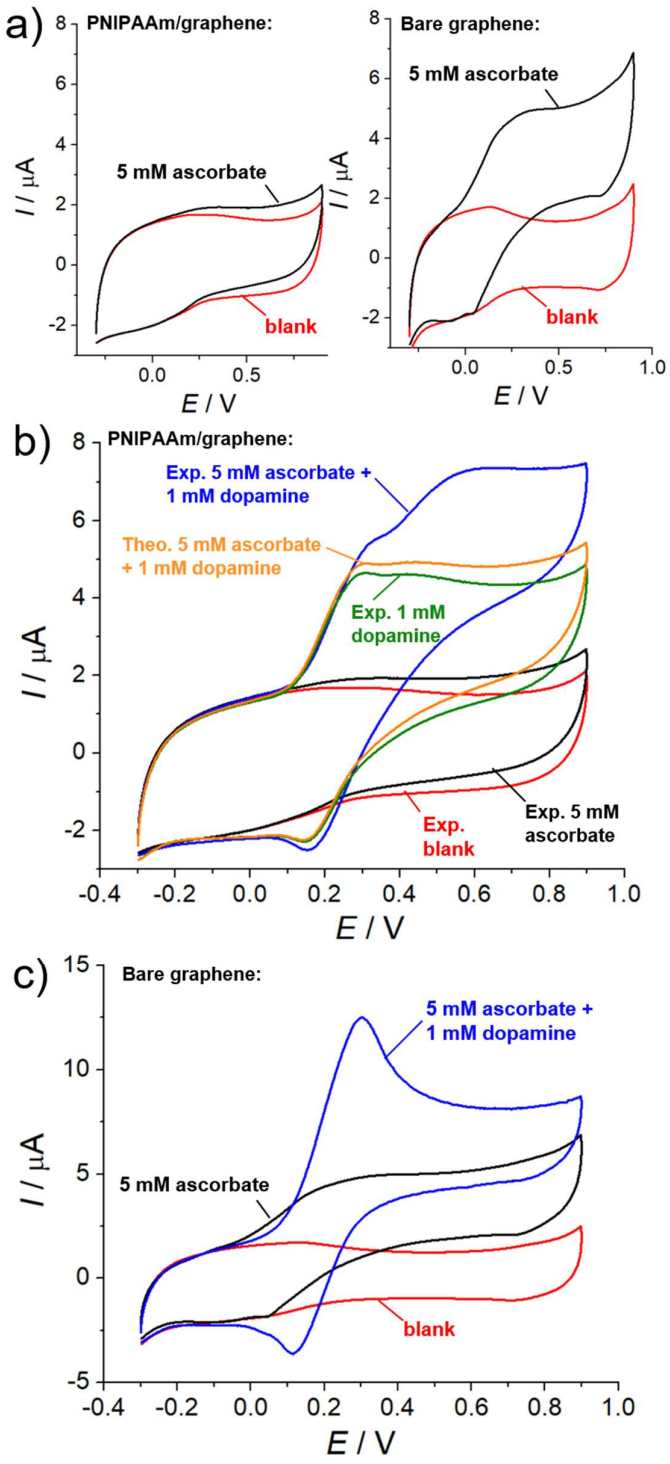

Fig. S6-4. a) Comparison of PNIPAAm-coated and non-coated graphene electrodes (Grid-3) for in PB (pH 7.4) solutions with (black curve) and without (red, blank) 5 mM ascorbate. b) CVs of Fig. 5b of the main article using thus a PNIPAAm/graphene electrode (Grid-3), with graphical addition of the theoretical curve for 1 mM dopamine and 5 mM ascorbic acid, calculated by considering the background-corrected curves for the individual solution. c) Use of a bare graphene electrode for the detection of dopamine in presence of ascorbate. 1 mM dopamine and 5 mM ascorbic acid in PB with pH 7.4 (blue curve), 5 mM ascorbic acid in PB with pH 7.4 (black) and only PB with pH 7.4 (red).