Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

An Array of Individually Addressable Micro-needles for Mapping pH Distributions

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FIGURE S1

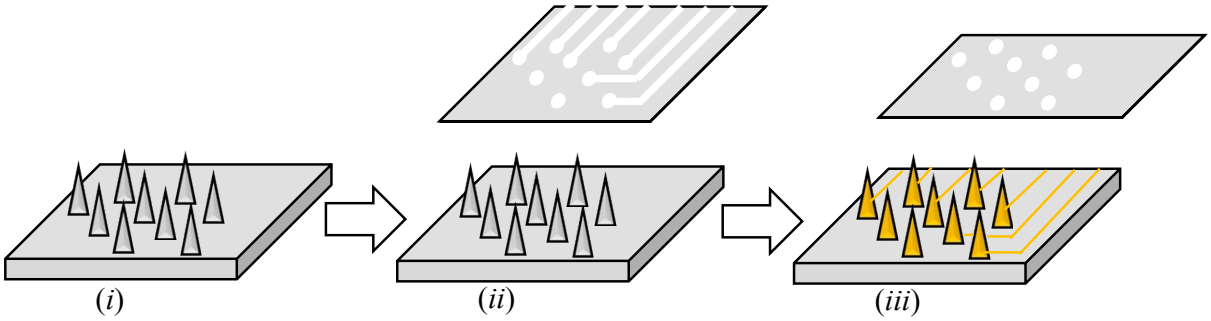

Figure S1. Stepwise procedure for gold patterning onto the surface of the (*i*) microneedles substrate. (*ii*) A 500 µm Mylar® stencil was laser micro-machined to provide apertures in correspondence of the needles and conductive tracks. The stencil was positioned on top of the substrate which was then gold coated using a sputter coater. (*iii*) The stencil was lifted and a Mylar® sheet laminated together with a double adhesive was laid onto the coated surface thus to leave needles and conductive pads exposed. Dimensions of the sketch are not in scale.

FIGURE S2

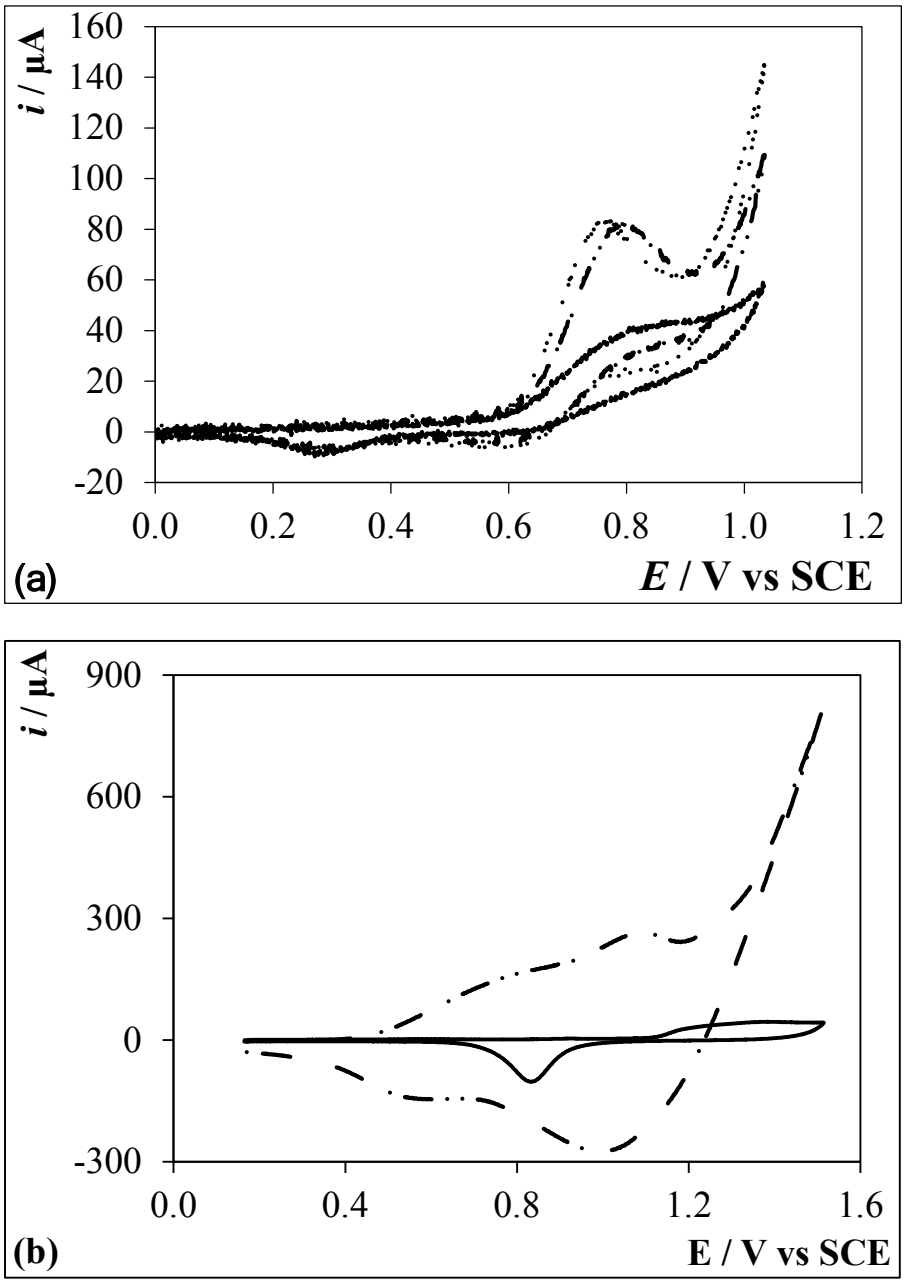

Figure S2. (a) Voltammograms obtained during the (—) 1st, (— · · —) 2nd (· · ·) and 3rd scans of an Au-coated needle immersed in the IrOx plating solution. The peak current increases during these scans, *i.e.,* 41, 78 and 83 µA, respectively and the peak potential shifts negatively with the scans, ~0.83, 0.79 and 0.76 V, respectively. Scan rate was 50 mVs^{-1} and a Pt coiled wire was used as counter electrode. (b) Cyclic voltammograms of (—) Au-coated and (— · · —) IrOx-coated needles immersed in a 0.5 M H_2SO_4 solution. The voltammograms of the former contains two distinctive redox couples which have been ascribed to IrO_2/Ir_2O_3 (E^0 ~ 0.65 V) and to higher valent oxide (E^0 ~ 1.05 V) transitions.

FIGURE S3

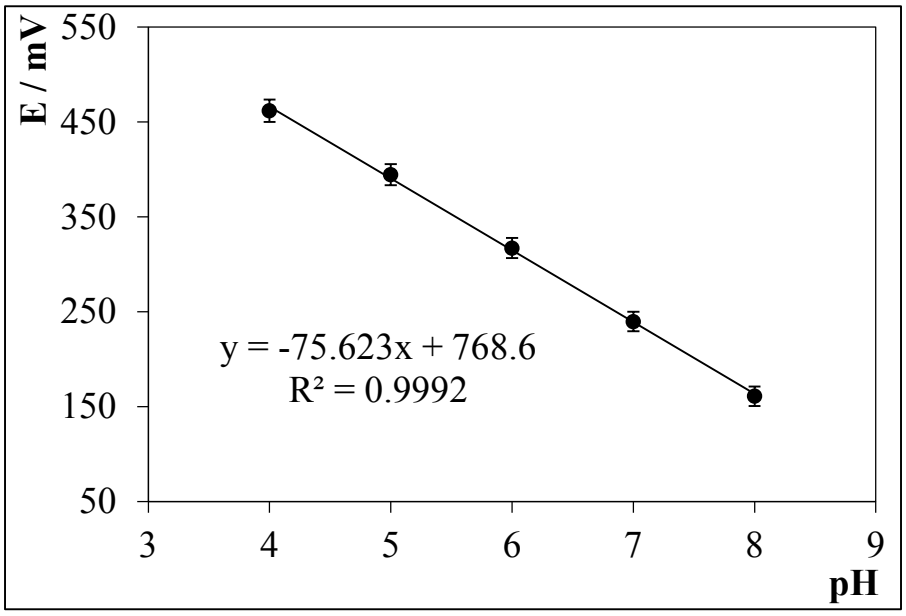

Figure S3. Calibration plot of an array of microneedles which were coated by IrOx deposited by applying a potential of 0.935 V for 600 s. Δ*E* values between the sensor and a double junction Ag/AgCl reference electrode were measured with the electrodes dipped in buffer solutions of pH 4, 5, 6, 7 and 8 during 3 minutes. Each point in the plot represents the Δ*E* obtained by averaging the values of the potential bias of the individual needles (n=7). Error bars in the graph represent the standard deviation.

Table S-1. Individual values of slope and offset as calculated from the linear regression carried out from the calibration of two microneedles array substrates. Each substrate consists of 7 IrOx-coated individually addressable needles. IrOx was deposited from the plating solution by applying a potential equal to 0.835 V vs SCE. The parameter *t* stands for time, i.e., days from the electrodeposition of the IrOx coating.

	Array A (*E*=0.835V)							**Array B (*E*=0.835V)**							
t	**N1**	**N2**	**N3**	**N4**	**N5**	**N6**	**N7**	**N1**	**N2**	**N3**	**N4**	**N5**	**N6**	**N7**	
1	74.9	75.7	75.6	76.0	75.0	75.8	75.1	74.2	74.5	74.5	75.0	74.4	74.0	73.9	**Slope**
3	69.1	70.2	69.0	69.5	68.6	68.5	68.0	67.8	67.7	67.7	68.1	67.5	67.6	67.3	
5	67.6	67.7	67.8	67.9	67.5	67.2	64.5	64.7	65.8	65.8	65.8	65.9	66.0	65.9	
1	741.8	763.3	749.2	760.5	738.4	757.1	743.4	721.0	734.0	734.0	741.5	734.3	724.7	720.3	**Offset**
3	612.9	642.2	606.1	613.7	603.6	600.7	593.8	580.6	578.9	578.9	588.0	576.1	578.1	575.5	
5	547.1	545.5	545.5	546.1	553.2	545.6	505.3	535.5	533.8	533.8	531.1	539.1	539.6	546.7	
1	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	**R^2**
3	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	
5	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	

Table S-2. Individual values of slope and offset as calculated from the linear regression carried out from the calibration of two microneedles array substrate. Each substrate consists of 7 IrOx-coated individually addressable needles. IrOx was deposited from the plating solution by applying a potential equal to 0.935 V vs SCE. The parameter *t* stands for time, i.e., days from the electrodeposition of the IrOx coating.

	Array C (*E*=0.935V)							Array D (*E*=0.935V)							
t	**N1**	**N2**	**N3**	**N4**	**N5**	**N6**	**N7**	**N1**	**N2**	**N3**	**N4**	**N5**	**N6**	**N7**	
1	75.3	75.5	75.5	76.6	75.3	76.4	74.7	74.1	73.3	74.6	74.2	73.4	73.7	73.7	**Slope**
3	68.4	67.8	68.3	68.5	69.9	67.6	66.1	67.9	67.6	67.6	66.5	67.1	66.7	67.2	
5	66.2	64.5	65.0	64.1	66.6	65.8	65.3	66.1	66.0	65.3	65.3	65.1	65.8	65.9	
1	767.5	756.1	778.4	776.8	774.2	781.9	745.4	727.8	718.7	743.8	733.1	721.8	738.7	732.5	**Offset**
3	599.4	591.0	611.4	603.8	632.9	610.0	590.7	580.7	572.4	570.3	559.8	569.4	570.0	576.1	
5	544.0	517.4	527.3	524.6	546.8	542.5	552.6	549.1	543.5	533.3	535.6	540.8	541.0	550.9	
1	0.999	0.999	0.999	0.999	1.000	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	**R^2**
3	0.999	0.999	0.999	0.999	1.000	0.999	0.999	0.999	0.999	0.999	0.999	0.999	1.000	0.999	
5	0.999	0.999	1.000	1.000	1.000	1.000	1.000	0.999	0.999	1.000	0.999	0.999	0.999	1.000	

Table S-3. Individual values of slope and offset as calculated from the linear regression carried out from the calibration of two microneedles array substrate. Each substrate consists of 7 IrOx-coated individually addressable needles. IrOx was deposited from the plating solution by applying a potential equal to 1.035 V vs SCE. The parameter *t* stands for time, i.e., days from the electrodeposition of the IrOx coating.

	Array E (*E*=1.035V)							Array F (*E*=1.035V)							
t	**N1**	**N2**	**N3**	**N4**	**N5**	**N6**	**N7**	**N1**	**N2**	**N3**	**N4**	**N5**	**N6**	**N7**	
1	72.8	71.5	71.5	71.8	69.0	72.3	72.6	70.8	70.5	70.0	70.8	66.9	71.5	74.7	**Slope**
3	67.2	69.6	67.5	68.9	68.4	68.6	50.4	63.4	66.5	66.9	62.4	65.1	66.5	68.4	
5	64.4	52.8	64.8	65.4	66.7	65.9	50.0	62.0	65.5	64.5	61.8	63.6	64.1	65.9	
1	699.6	697.0	686.6	686.0	661.7	691.2	711.4	705.4	708.4	713.4	723.0	696.6	727.2	748.2	**Offset**
3	600.6	653.1	613.0	638.7	605.3	637.0	497.3	521.5	569.1	574.8	603.3	577.7	601.0	600.8	
5	567.8	489.8	568.8	548.9	572.8	57.3	488.8	518.5	541.3	543.4	526.5	534.0	540.8	552.6	
1	0.998	0.997	0.998	0.997	0.998	0.998	0.998	0.998	0.997	0.996	0.996	0.997	0.997	0.999	**R^2**
3	0.999	0.999	0.999	0.999	1.000	0.999	0.998	0.999	0.999	0.999	0.999	0.998	0.997	0.999	
5	1.000	0.998	1.000	0.999	1.000	1.000	0.998	0.998	1.000	1.000	0.997	0.999	1.000	1.000	

FIGURE S4

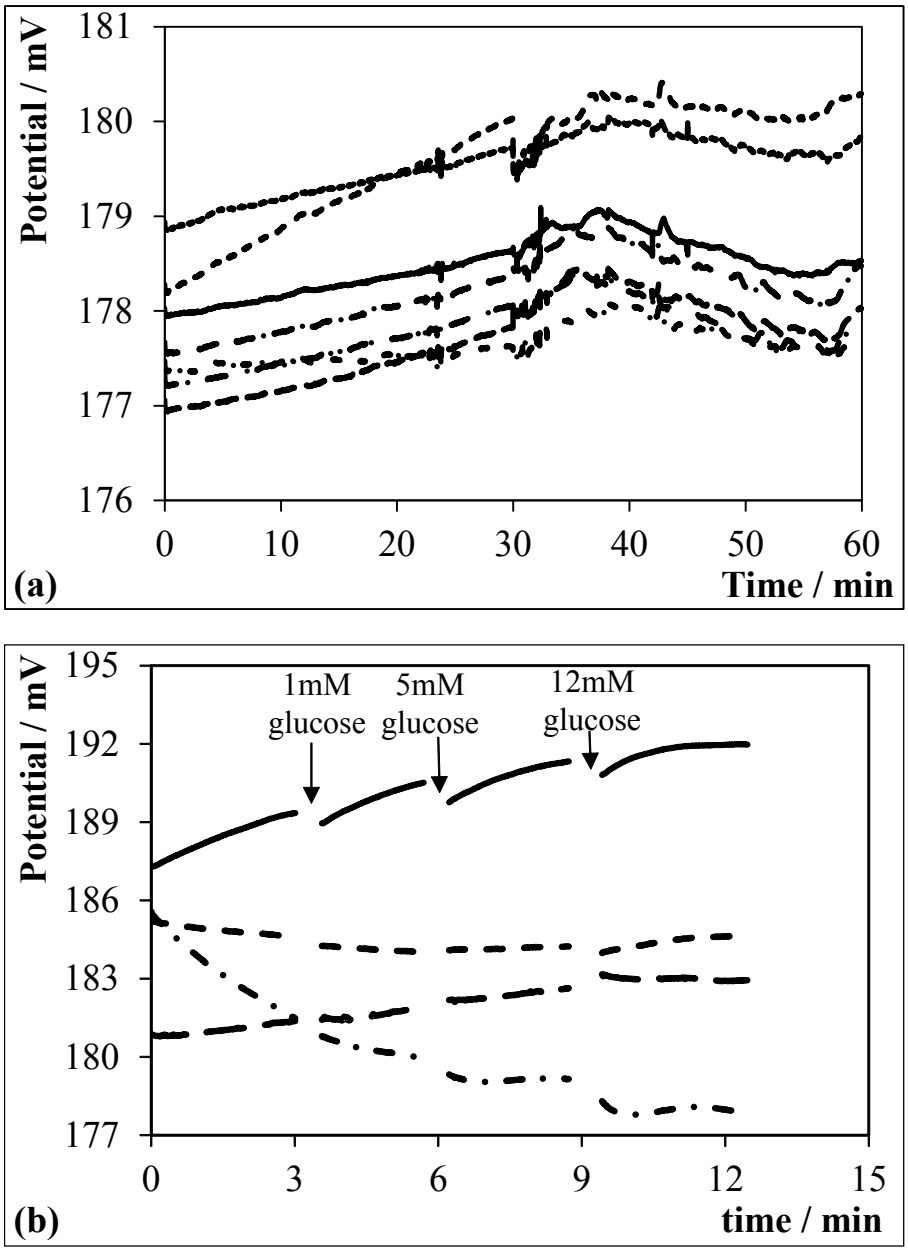

Figure S4. Each line corresponds to the potentiometric trace of IrOx-coated needles which were immersed in a phosphate buffer (pH=6.80 ± 0.05) containing 0.1 M KNO_3. (a) After 30 minutes immersion the solution was replaced with an identical one which was saturated with N_2. (b) The buffer was spiked with 0.96 M aqueous glucose solution at the time indicated by the arrows to obtain a concentration equal to the ones reported in the graph.

FIGURE S5

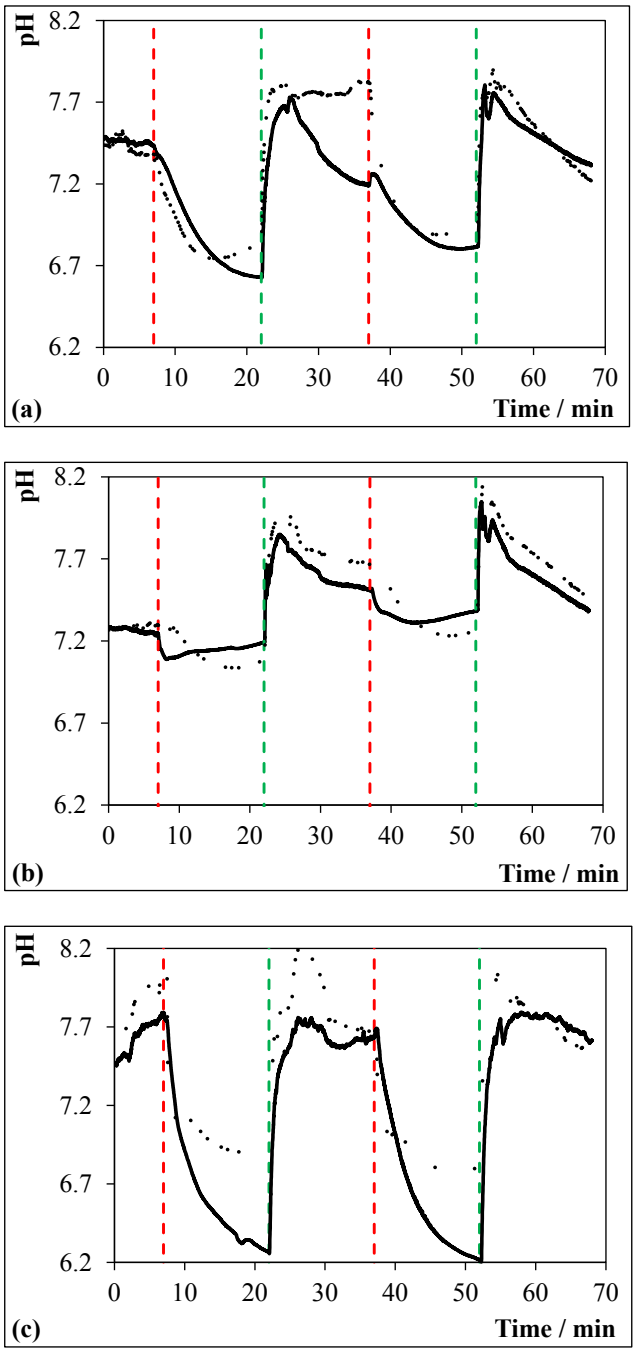

Figure S5. Traces of pH as measured by the microneedles (a) N3 (—) and N7 (···) belonging to group *i*, (b) N1 (—) and N2 (···), group *ii* and (c) N5 (—) and N4 (···), group *iii*. Microneedles were inserted into an explanted heart and after 8 minutes background recording, the rat heart underwent two cycles of global heart ischemia/reperfusion. Ischemia occurred at t=8 min and 38 min while reperfusion was started at t=22 min and 52 min as indicated by the red and green dashed vertical lines, respectively.