Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

ON/OFF Switching of Silicon Wafer Electrochemistry by pH-Responsive Polymer Brushes

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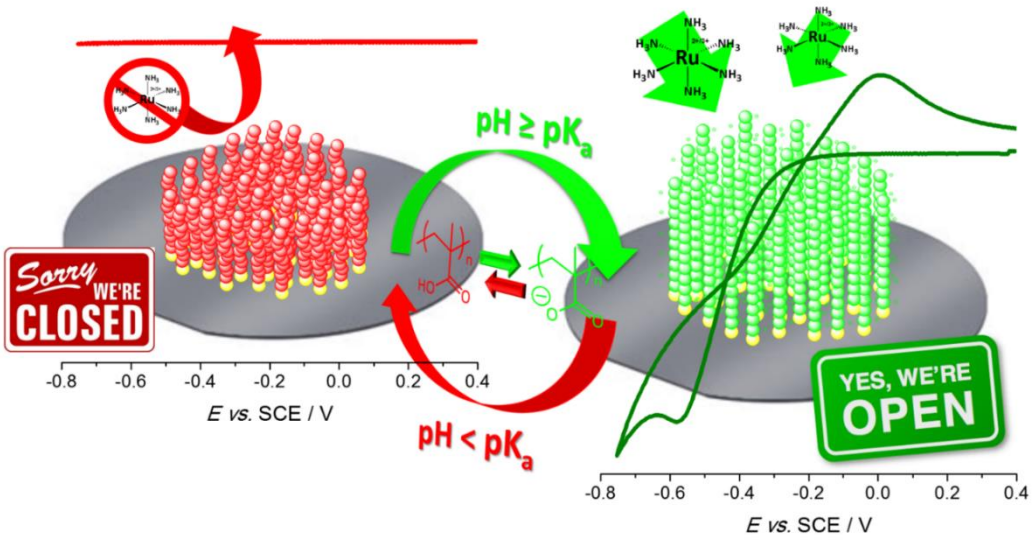


ESTIMATION OF THE BRUSH PARAMETERS

The grafting density σ of self-assembled monolayers and of polymer chains on a surface can be estimated according to eq. S1:

$$\sigma = \frac{h\rho N_A}{M_n} \qquad \text{(S1)}$$

where h is the layer thickness, ρ is the layer density, N_A is the Avogadro's number and M_n is the molecular weight.

For a self-assembled monolayer of the BIB-APTES initiator on silicon, a surface density $\sigma_{initiator}$ of ~ 4 molecules nm^{-2} was obtained from eq. S1 using a thickness of 2 nm (determined by ellipsometry), a density of 1.17 g cm^{-3} and a molecular weight of 286 g mol^{-1} (corresponding to the fully hydrolyzed silane molecule).

Since the average initiation efficiency for similar systems[1] is ~ 10 %, it is plausible to affirm that a surface density of chains $\sigma_{brushes}$ of at least 0.4 chains nm^{-2} has been achieved, which is a typical value for polymer brushes. An average distance between grafting sites D of ~ 0.71 nm can be calculated, under the assumption that each brush chain occupies a cylindrical volume with its base coincident with the grafting surface, according to eq. S2:[2]

$$D = \left(\frac{4}{\pi\sigma}\right)^{1/2} \qquad \text{(S2)}$$

Assuming a density of 1.18 g cm^{-3} for PMAA, the calculated molecular weight M_n values for the ultrathin (14 nm) and ultrathick (1 μm) brushes are respectively 2.3 x 10^4 g mol^{-1} and 1.7 x 10^6 g mol^{-1}.

Solvent	*pH*	*Solvent content [%]*	*Refractive index n*	*Thickness [nm]*	*MSE [nm]*	*Average thickness [nm]*	*Average MSE [nm]*	*Swelling [%]*
Dry	-	0.0	1.5226-1.4601	13.7	1.6	13.8	1.4	0
		0.0	1.5226-1.4601	14.2	1.3			
		0.0	1.5226-1.4601	13.6	1.3			
HCl	1	53.1	1.4328-1.3875	33.9	1.9	34.5	1.7	149
		55.7	1.4321-1.3870	35.6	1.7			
		53.0	1.4279-1.3836	33.9	1.4			
H_2O	7	76.7	1.3926-1.3550	41.1	1.8	40.7	1.6	194
		76.6	1.3926-1.3550	41.0	1.8			
		73.9	1.3972-1.3588	40.1	1.3			
NaOH	13	90.0	1.3705-1.3370	69.1	1.8	69.2	1.7	400
		89.3	1.3715-1.3379	69.0	1.5			
		90.1	1.3701-1.3367	69.4	1.7			

Table S1. pH-dependent swelling behavior of ultrathin PMAA brushes probed by spectroscopic ellipsometry.

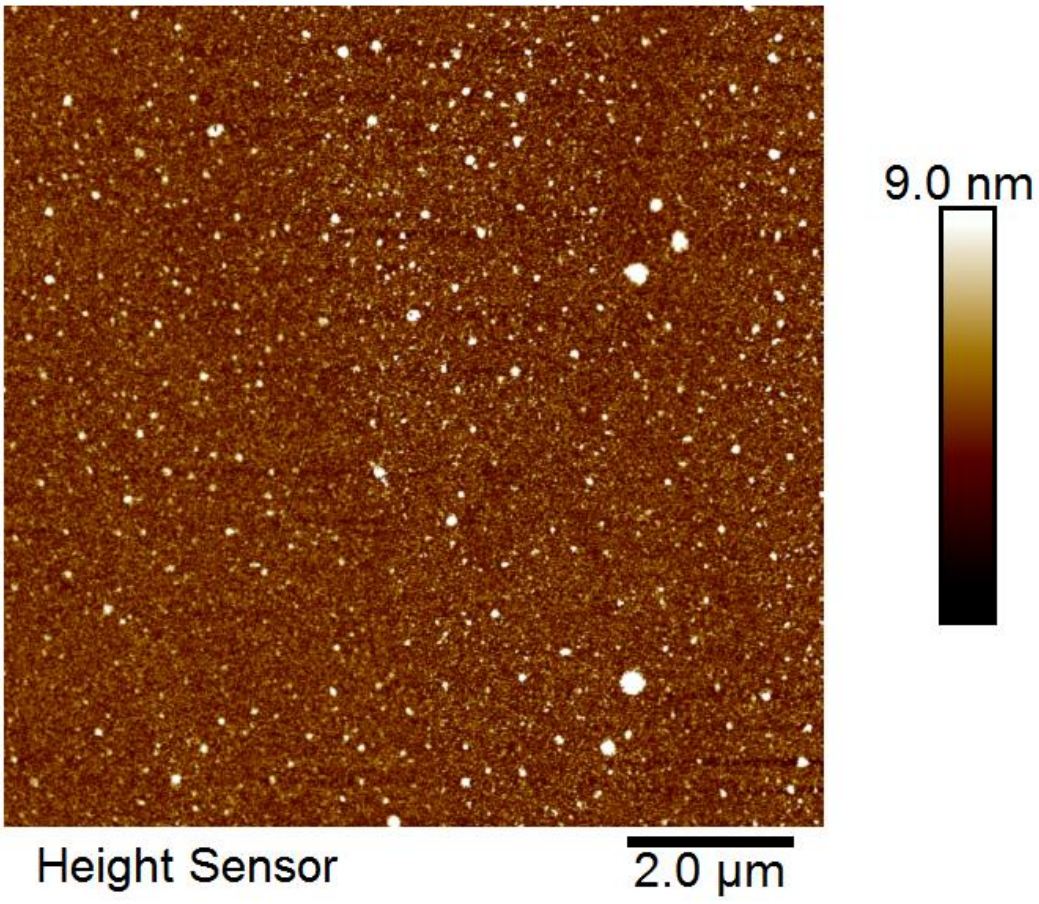


Figure S1. AFM image of a 10 nm-thick PMAA brushes used to measure roughness.

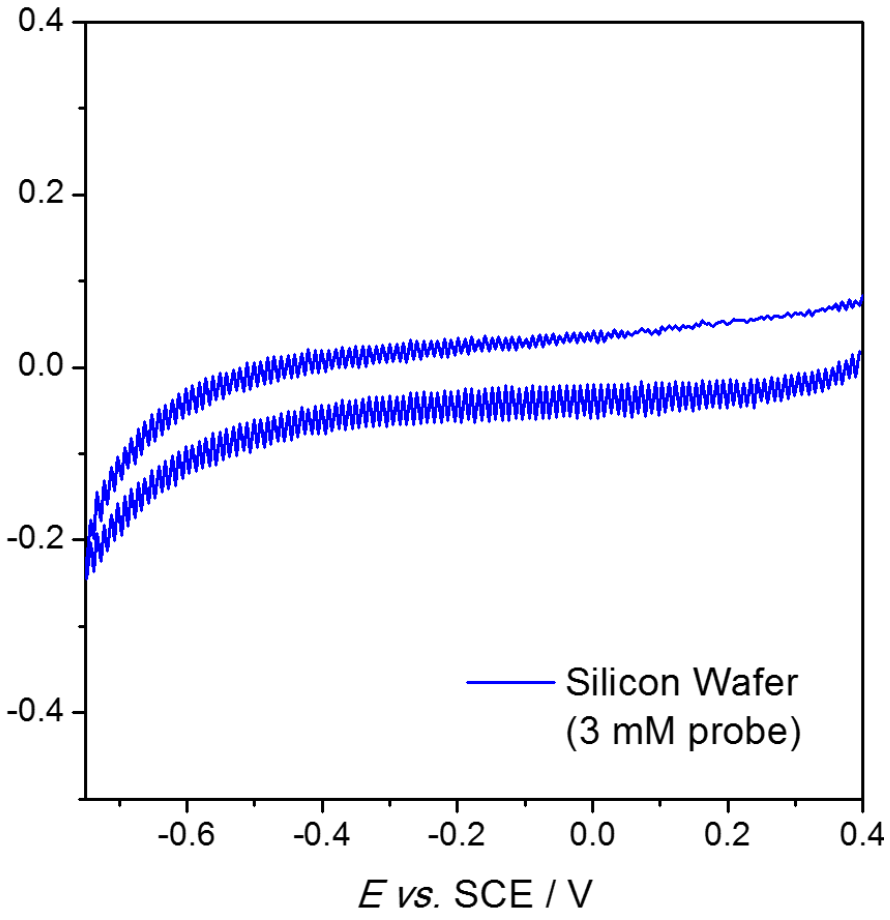


Figure S2. Cyclic voltammetry (CV) of native oxide-coated silicon wafer performed in presence of 3 mM ruthenium(III) hexamine showing that there is no electrochemical response for this kind of electrode.

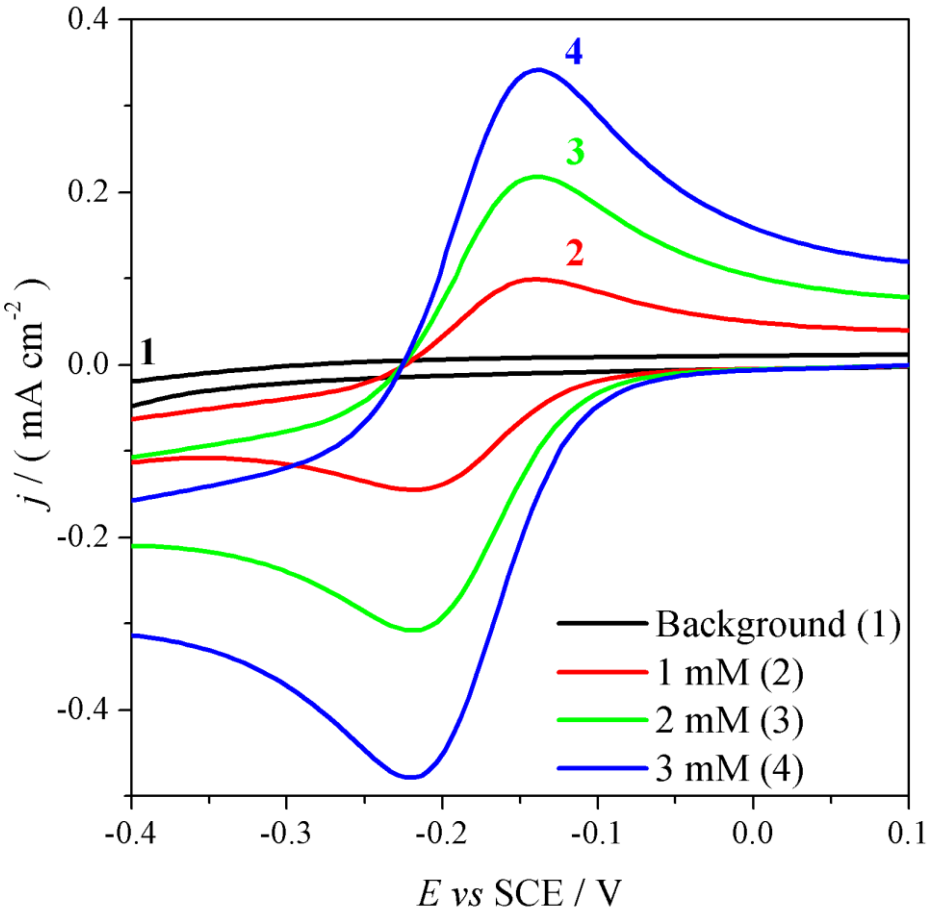
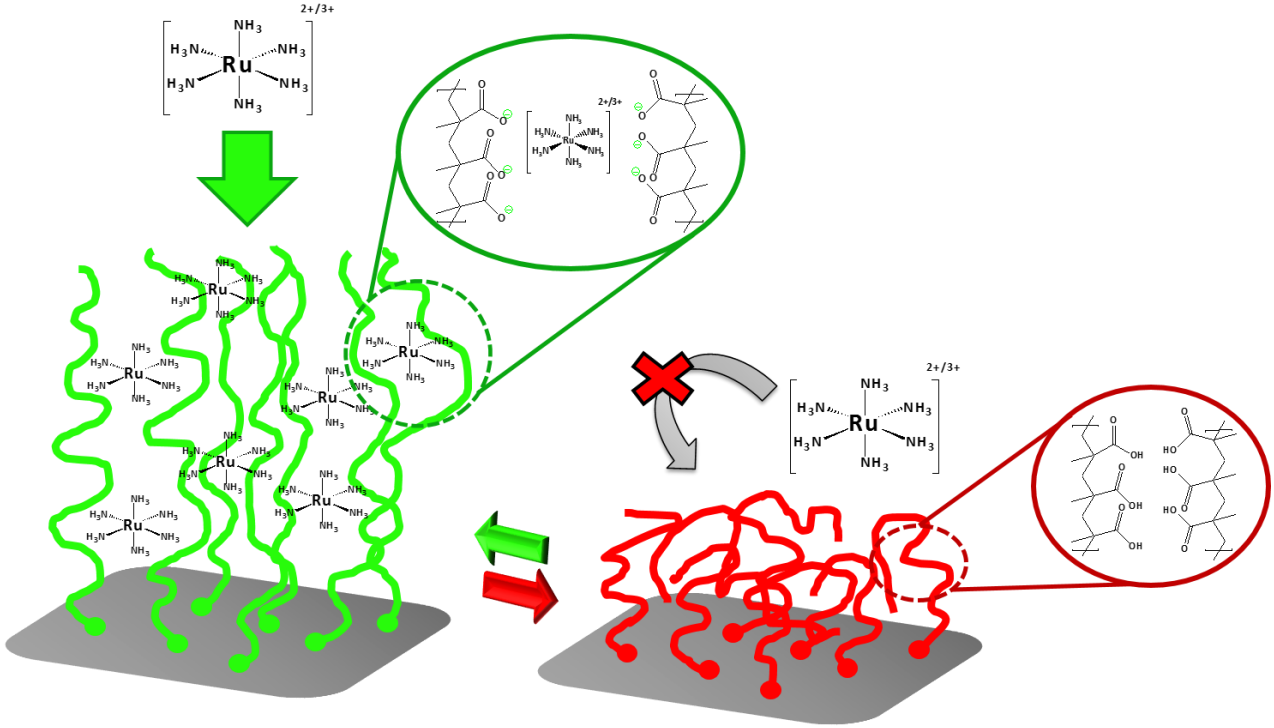


Figure S3. Cyclic voltammetry (CV) scans, obtained using glassy carbon as a "conventional" working electrode, showing the typical reduction and oxidation peaks of the ruthenium(III) hexamine redox probe. All other experimental conditions were the same used to analyze the PMAA brushes-modified silicon wafer electrodes.



Scheme S1. Schematic representation of the effect of pH on the diffusion of the ruthenium probe inside the PMAA brushes: left, pH 10; right, pH 2.

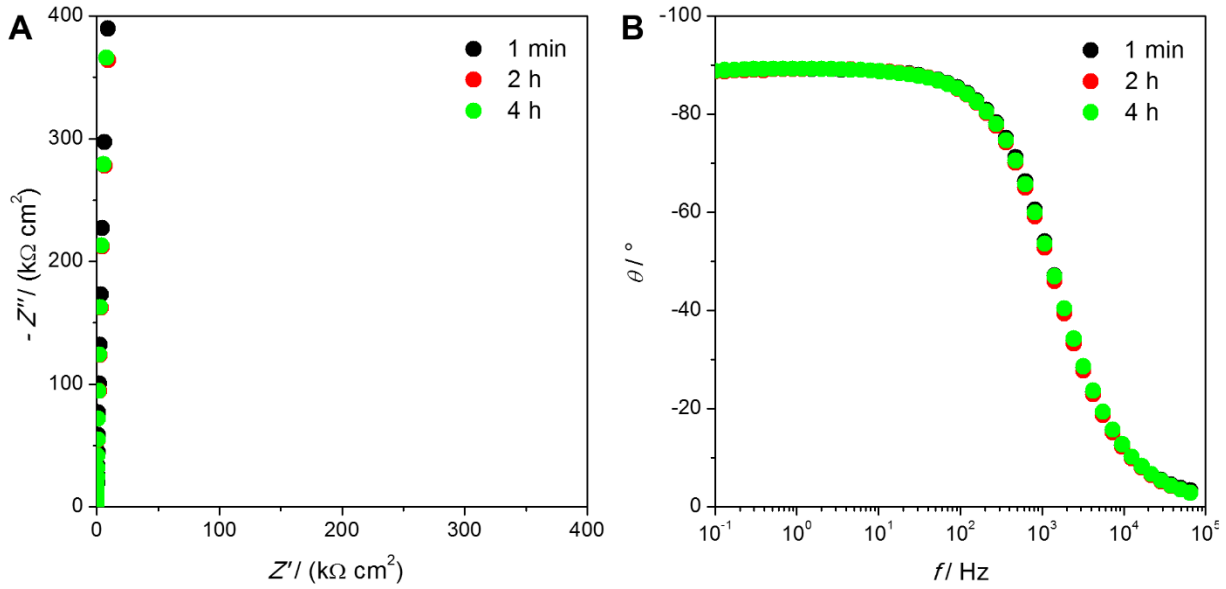


Figure S4. EIS investigation of the swelling of ultrathin PMAA brushes: (a) complex plane and (b) Bode plots. To collect data, the dry brushes were immersed in the supporting electrolyte (pH 7) and the EIS experiments performed after 1 min, 2 h and 4 h.

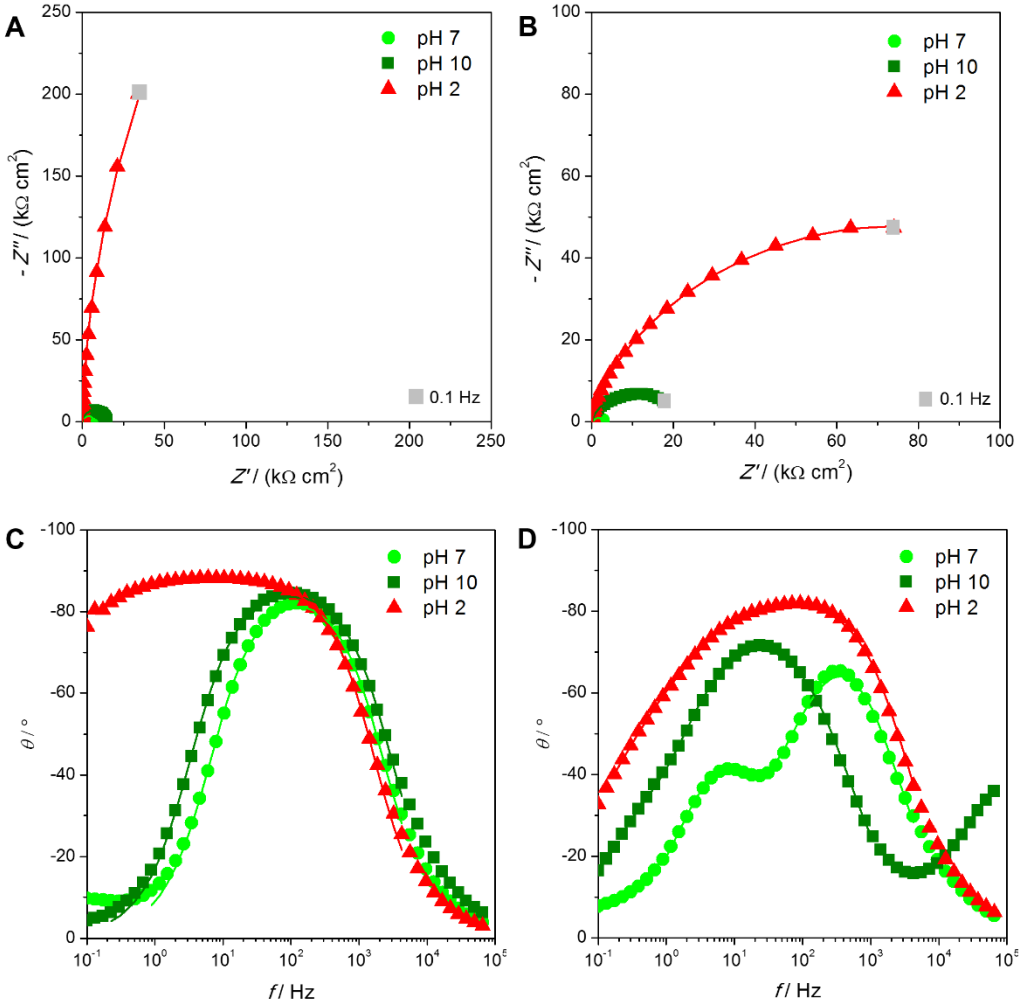


Figure S5. The original (not rescaled) EIS plots for a) ultrathin and b) ultrathick PMAA brushes, along with their corresponding Bode plots (c, d) obtained in the presence of the redox probe.

REFERENCES

1. D. M. Jones, A. Brown and W. T. S. Huck, *Langmuir* 2012, **18**, 1265–1269.
2. A. Samadi, S. M. Husson, Y. Liu, I. Luzinov and S. M. Kilbey II, *Macromol. Rapid Commun.* 2005, **26**, 1829–1834.