SUPPLEMENTARY INFORMATION

Plasma Polymerised PolyOxazoline Thin Films for Biomedical Applications

M.N. MacGregor-Ramiasa,[a#] A.A. Cavallaro[a#] , A. Mierczynska[b], S.N. Christo [c], J.M. Gleadle[d], J. D. Hayball[c] and K. Vasilev[a*]

[a] Mawson Institute, University of South Australia, Mawson Lakes, SA 5095, Australia.

[b] The Australian Wine Research Institute, Hartley Grove Cnr Paratoo Road, Urrbrae (Adelaide) SA 5064, Australia

[c] School of Pharmacy and Medical Sciences, University of South Australia, SA 5000, Australia

[d]Renal Department, Flinders Medical Centre, Flinders University School of Medicine, Bedford Park, Adelaide, South Australia 5042, Australia

 # Equal contribution

***Author for correspondence**

Capacity of plasma deposited Pox coatings to bind COOH functionalised gold nanoparticles

Gold nanoparticles were synthesized following methods previously established [28]. Briefly 15nm nanoparticles were synthesized by citrate reduction of HAuCl4 and subsequently functionalised with carboxylic acid using 2-mercaprosuccinic acid.

In order to investigate the reactivity of POx plasma polymer films with carboxylic acid chemical groups, glass coverslips coated with plasma deposited POx were incubated with the so obtained

COOH-functionalised gold nanoparticles in 24 well plates for 6h at room temperature. The gold nanoparticles suspension was then aspirated and the coverslips rinsed 3 times with MilliQ water.

The nature of the bond between the COOH functionalised gold nanoparticles and the POx coating was challenged by washing for 1h with a surfactant solution (SDS 1v %). Finally, the substrates were thoroughly rinsed with large amount of flowing MilliQ water and dried with nitrogen flow. Alylamine coated substrates, on which the gold nanoparticles adsorption is expected to be driven by electrostatic interactions, were used as control surfaces.

In order to quantitatively measure gold nanoparticles binding and desorption the surface were analysed via XPS. In Figure SI1, we report the atomic percentage of gold for control AA coated substrate, and POx 30W and 50W.

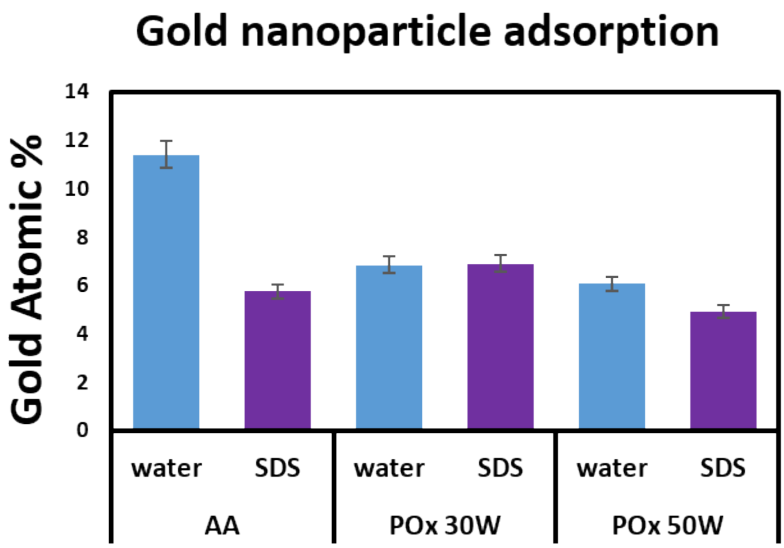

Figure SI1: Gold atomic concentration in % for AA, POx 30W and Pox 50W samples after rinsing with water or SDS 1v% solution.

Gold nanoparticles adhere to all surfaces, reaching up to 12% coverage on the alylamine coated surfaces, and approximately 6% on the POx coated surfaces. Yet, it is clear from the XPS measurement that almost 50% of the gold adsorbed on the AA coated samples is lost after SDS wash. This result indicates that some of the gold nanoparticles binding on the AA samples are doing so via reversible electrostatic interactions which are readily disrupted by exposure to surfactants and concentrated salt solutions. On the other hand, the POx substrate bear little to no loss following SDS wash: a slight decrease in the amount of gold nanoparticle is observed after SDS rinse for 50W samples, while in these conditions the nanoparticle binding is unaltered on the 30W films which suggest a strong covalent binding. In the case of the 50W films, this could be that two different adsorption mechanism are at play, namely electrostatic adsorption and covalent irreversible binding. Although further investigations are required, these set of results seem to indicate that the reaction of POx films with COOH-groups result in irreversible nanoparticle adsorption.

Polyacrylic reaction with plasma deposited POx coatings

Plasma coated glass coverslips were initially rinsed with MilliQ water before incubating with 1w% polyacrylic acid (PAA) solution for 1h in 24 well plates. After aspirating the PAA solution, the substrate were rinsed 3 times with MilliQ water, before washing with SDS 1v%, as described above. Finally all samples were thoroughly rinsed with large amount of MilliQ water and dried with nitrogen flow. Once again, Alylamine samples were used as controls.

The samples were then analysed via XPS. The high resolution C1S spectra providing the carbon environment of the various samples before exposure to PAA, after water rinse and after SDS rinse are shown in Figure SI2.

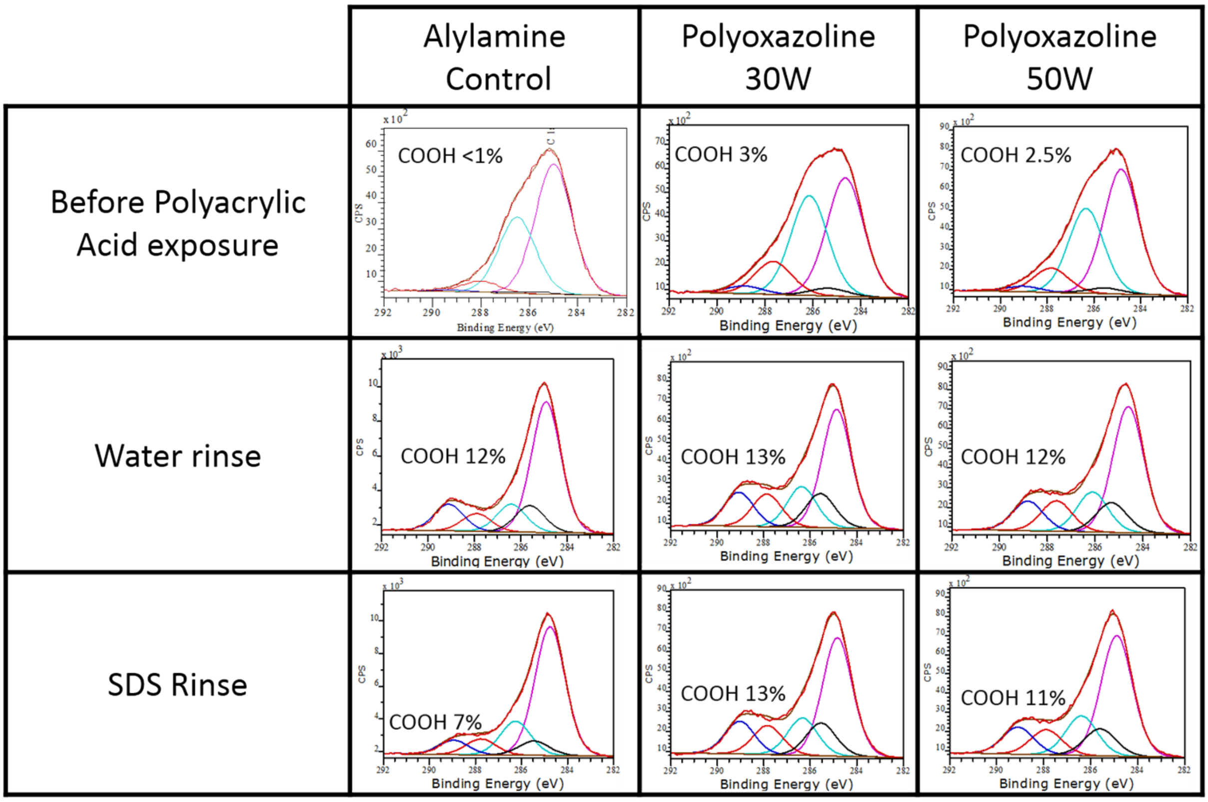

Figure SI2: C1s spectra of AA, POx 30W and Pox 50W samples before exposure to Polyacrylic acid and after rinsing with water or SDS 1v% solution.

The increase in carboxylic acid function occurring for all samples after exposure to PAA confirm the binding of the PAA molecule to the substrate. Both Alylamine and POx surfaces reached similar COOH content (namely AA: 12% $\pm$ 1, POx 30W 13% $\pm$ 1 and POx 50W 12% $\pm$ 1). Yet, once again, a significant loss, namely 42%, is observed for the alylamine surfaces after exposure to SDS (1%) solution, while no significant loss is observed from the POx surfaces.

This results together with those of FTIR, XPS, and Protein and Gold nanoparticles binding suggest that at least a small amount of oxazoline rings are retained during the plasma polymerisation process and able to covalently bind carboxylic acid functions.

Plasma deposited POx coatings topography

Plasma deposited POx films surface topography was investigated via AFM. The coating were homogeneous and molecularly smooth, with RMS roughness below 0.5nm. A typical AFM image of POx films deposited at 50W is shown in Figure SI3.

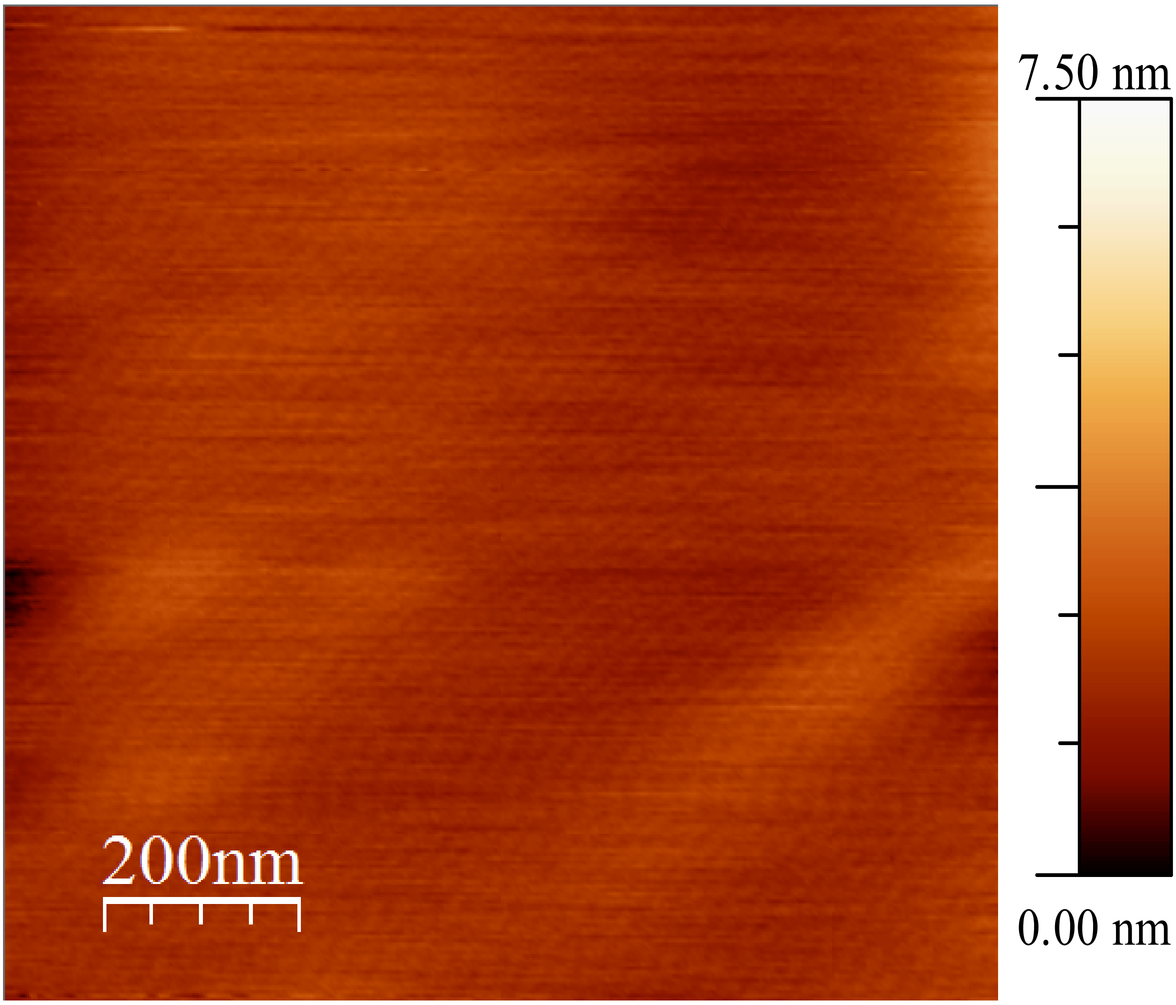

Figure SI3: AFM image of Plasma deposited POx film, 50W, 5min. RMS roughness: 0.3102nm

Size scale is Z-axis