

## Electronic Supplementary Information (ESI)

### Directly observed Au-S bond breakage due to swelling of the anchored polyelectrolyte

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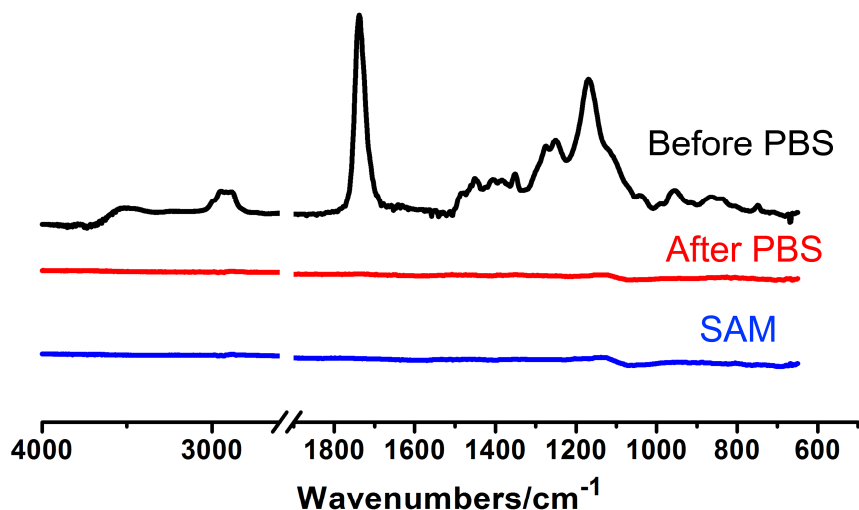
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#### Materials

The initiator thiol ( $\omega$ -mercaptoundecyl bromoisobutyrate), diluent thiol (11-Mercaptoundecyl)tri(ethylene glycol) (EG-thiol), QCM chips were purchased from HRBio (Beijing, China). The mole ratio of initiator in the mixed thiols solution  $\chi_I^{Sol}$  was defined as  $\chi_I^{Sol} = M_{initiator}/(M_{initiator} + M_{diluent})$ . Oligo(ethylene glycol) methacrylate (OEGMA,  $M_w = 526$ ), 2-hydroxyethyl methacrylate (HEMA), anhydrous N, N'-dimethylformamide (DMF), succinic anhydride, 4-(dimethylamino) pyridine (DMAP) were purchased from Aldrich and used as received.

#### Surface characterizations

**Fourier transform infrared spectrometer (FTIR).** FTIR adsorption spectra were obtained with a Thermo Nicolet 6700 Fourier transform infrared spectrometer (Thermo Fisher Scientific, USA), equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector and a Smart Apertured Grazing Angle (SAGA) accessory.

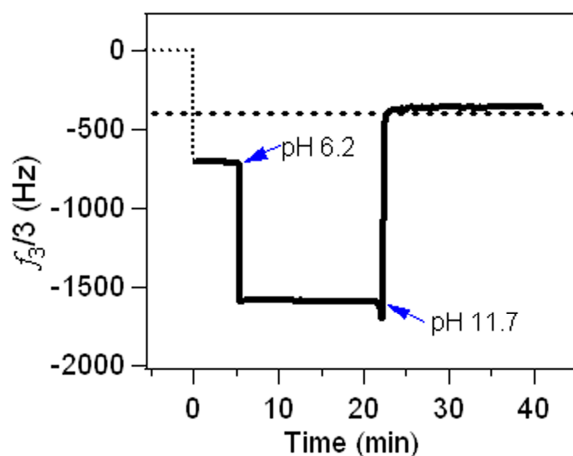


**Fig. S1.** FTIR spectrum of the carboxylated poly(OEGMA-co-HEMA) coating before and after PBS exposure. A  $T_{\text{COOH, dry}} = 80$  nm coating was removed after the chip was exposed to PBS and exhibited a similar spectrum with mixed self-assembled monolayer (SAM) of initiator and diluent.

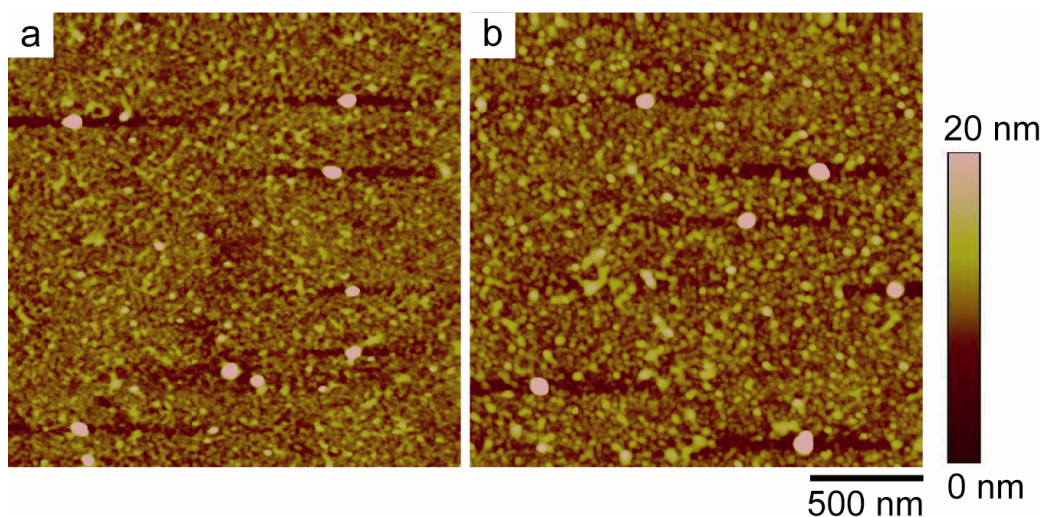
**X-ray photoelectron spectrometer (XPS).** XPS (AXIS Ultra by Kratos Analytical, UK) was used to determine the chemical composition of the modified surfaces. Monochromatic Al KR X-rays (1486.7 eV) were employed.

**Table S1.** Elemental composition of a  $T_{\text{COOH, dry}} = 85$  nm coating determined by XPS using  $90^\circ$  take off angles.

Samples	SAM	Carboxylated poly(OEGMA-co-HEMA)	
		Before PBS	After PBS
O <sub>1s</sub> (%)	12.8	30.7	9.3
C <sub>1s</sub> (%)	50.2	69.3	42.4
Au <sub>4f</sub> (%)	34.8	-	46.4
S <sub>2p</sub> (%)	2.0	-	1.9
Br <sub>3d</sub> (%)	0.2	-	-
C/O (%)	3.91	2.26	4.56



**Fig. S2.** Direct observation of *in situ* covalent bond breaking induced by MilliQ-water (pH = 11.7, adjusted with NaOH). The coating with T<sub>COOH, dry</sub> at 87 nm behaved differently upon exposure to MilliQ-water with different pH and was removed when exposed to MilliQ-water (pH = 11.7).



**Fig. S3.** AFM characterization of polyelectrolyte coatings from ultra-low initiator density ( $\chi_I^{Sol} = 0.001\%$ ). The surface morphologies presented were carboxylated poly(OEGMA-co-HEMA) (a) before and (b) after PBS (pH 7.4,  $[\text{Na}^+] = 150 \text{ mM}$ ) washing. There was no significant difference of the number of surface tethered polyelectrolyte chains, indicating carboxylated poly(OEGMA-co-HEMA) was not pulled off individually.

**Grafting density of polyelectrolyte coating.** Based on the previous reports,<sup>1,2</sup> it is found that the surface area of an initiator molecule immobilized on Au(111) surface with  $\chi_I^{Sol} = 100\%$  is  $21.4 \text{ \AA}^2$ . Thus for our system with  $\chi_I^{Sol} = 2.5 \%$  the surface area of an initiator molecule is  $856 \text{ \AA}^2$  (corresponding to the initiator density with  $0.116 \text{ chains/nm}^2$ ), which is much larger than the average cross sectional area of a polymer chain ( $\sim 180\text{-}200 \text{ \AA}^2$ ).<sup>2</sup> Therefore, the steric factors inhibiting polymer chains growing from every single initiator in the SAM can be omitted and it is reasonable to assume that the graft density of polymer is equivalent to the initiator density ( $0.116 \text{ chains/nm}^2$ ).

## References

1. A. Ulman, *Chem. Rev.*, 1996, **96**, 1533-1554.
2. D. M. Jones, A.A. Brown and W.T.S. Huck, *Langmuir*, 2002, **18**, 1265-1269.