Morphological Control of PbS Grown on Functionalized Self-Assembled Monolayers by Chemical Bath Deposition – Supporting Information

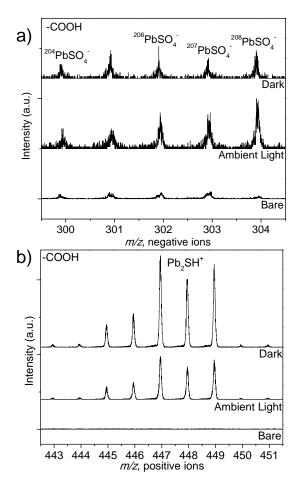
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3.1 Deposition of PbS on -COOH Terminated SAMs

Figure S1. High resolution TOF SIMS spectra centered at a) m/z 302 and b) m/z 447 after PbS chemical bath deposition for 85 mins at 45 °C and pH 11 on –COOH terminated SAMs. Depositions were either performed under ambient light or in the dark. Also shown for reference is the SIMS spectrum of the bare –COOH terminated SAM.

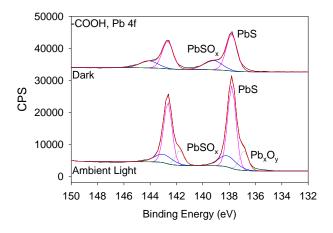


Figure S2. High resolution Pb4f XPS spectra after PbS chemical bath deposition for 85 mins at 45 °C and pH 11 on –COOH terminated SAMs. Depositions performed under anaerobic conditions in ambient light and in the dark. Data obtained using a PHI VersaProbe II, and the colored lines show the fit to the experimental data.

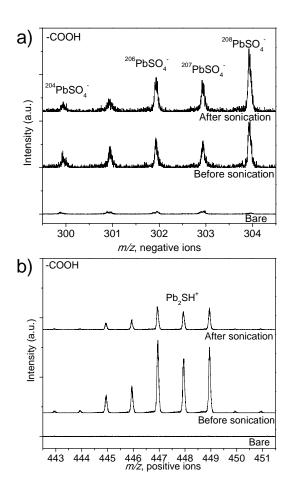


Figure S3. High resolution TOF SIMS spectra centered at a) m/z 302 and b) m/z 447 after PbS chemical bath deposition for 85 mins at 45 °C and pH 11 on –COOH terminated SAMs before and after sonication in deionized water for 2 mins. Also shown for reference is the SIMS spectrum of the bare –COOH terminated SAM.

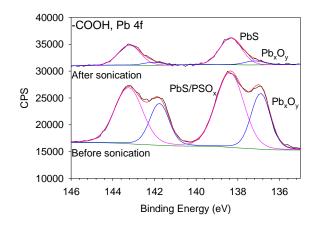


Figure S4. High resolution Pb4f XPS spectra after PbS chemical bath deposition for 85 mins at 45 °C and pH 11 on –COOH terminated SAMs before and after sonication in deionized water for 2 mins. The colored lines show the fit to the experimental data.

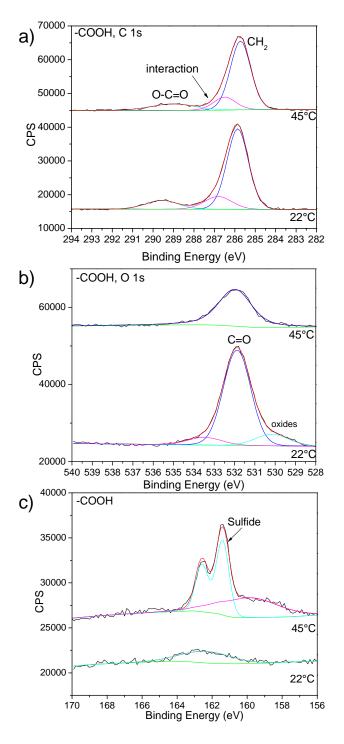


Figure S5. High resolution (a) C1s, (b) O 1s and (c) S 2p XPS spectra after PbS chemical bath deposition for 85 mins at pH 11 on –COOH terminated SAMs at 22 °C and 45 °C. After deposition the samples were sonicated in deionized water for 2 mins. The colored lines show the fit to the experimental data.

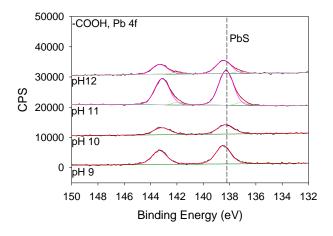


Figure S6. High resolution Pb4f XPS spectra after 85 mins PbS chemical bath deposition at 45 °C on –COOH terminated SAMs for bath pH from 9 to 12. After deposition the samples were sonicated in deionized water for 2 mins. The bath pH was varied from pH 9 to pH 12. The colored lines show the fit to the experimental data, and the dotted line at 138.2 eV (PbS) is shown as a guide to the eye.

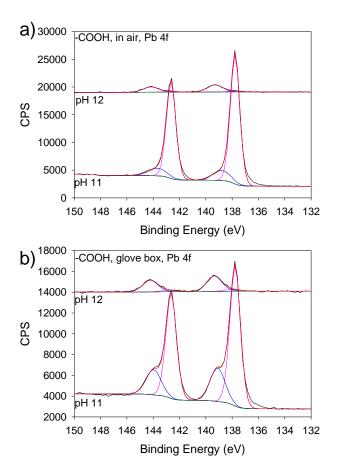


Figure S7. High resolution Pb4f XPS spectra after 85 mins PbS chemical bath deposition at 45 °C on –COOH terminated SAMs for bath pH 11 and 12. Depositions performed a) in air and b) under anaerobic conditions ("glovebox"). After deposition the samples were sonicated in deionized water for 2 mins. Data obtained using a PHI VersaProbe II, and the colored lines show the fit to the experimental data.

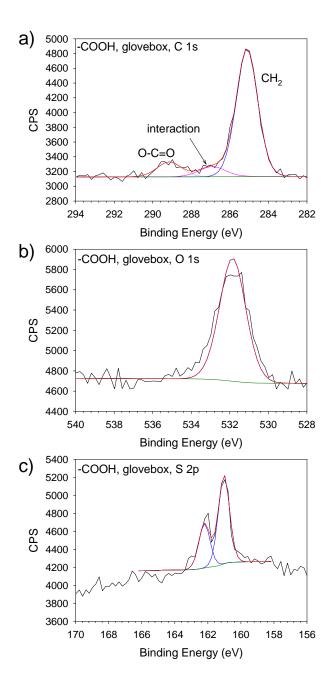


Figure S8. High resolution (a) C1s, (b) O 1s and (c) S 2p XPS spectra after PbS chemical bath deposition for 85 mins at pH 11 on –COOH terminated SAMs at 45 °C. Deposition performed under anaerobic conditions ("glovebox"). After deposition the samples were sonicated in deionized water for 2 mins. Data obtained using a PHI VersaProbe II, and the colored lines show the fit to the experimental data.

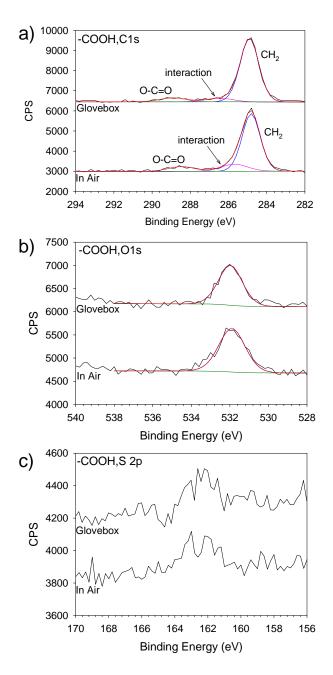


Figure S9. High resolution (a) C1s, (b) O 1s and (c) S 2p XPS spectra after PbS chemical bath deposition for 85 mins at pH 12 on –COOH terminated SAMs at 45 °C. Deposition performed in air and under anaerobic conditions ("glovebox"). After deposition the samples were sonicated in deionized water for 2 mins. Data obtained using a PHI VersaProbe II, and the colored lines show the fit to the experimental data.

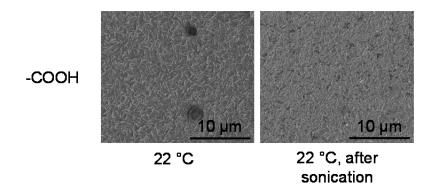


Figure S10. SEM images after PbS chemical bath deposition for 85 mins at 22 °C and pH 11 on –COOH terminated SAMs before and after sonication in deionized water for 2 mins.

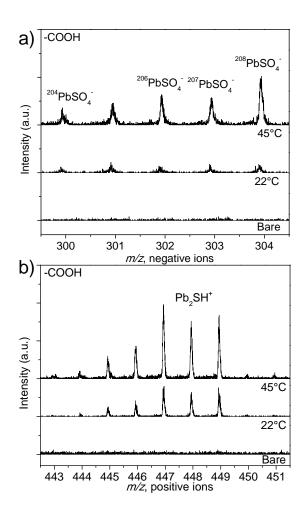


Figure S11. High resolution TOF SIMS spectra centered at a) m/z 302 and b) m/z 447 after PbS chemical bath deposition for 85 mins at pH 11 on –COOH terminated SAMs at 22 °C and 45 °C. Also shown for reference is the SIMS spectrum of the bare –COOH terminated SAM.

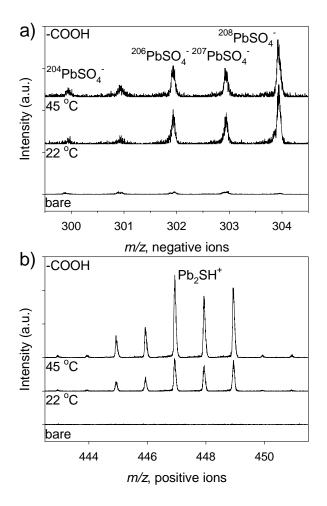


Figure S12. High resolution TOF SIMS spectra centered at a) m/z 302 and b) m/z 447 after PbS chemical bath deposition for 85 mins at pH 11 on –COOH terminated SAMs at 22 °C and 45 °C. After deposition the samples were sonicated in deionized water for 2 min. Also shown for reference is the SIMS spectrum of the bare –COOH terminated SAM.

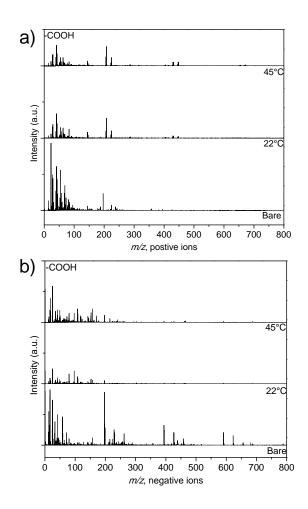


Figure S13. Positive and negative TOF SIMS spectra m/z 0-800 after PbS chemical bath deposition for 85 mins at pH 11 on –COOH terminated SAMs at 22 °C and 45 °C. Also shown are the spectra of the bare monolayer.

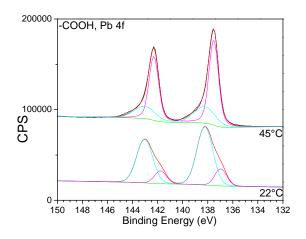


Figure S14. High resolution Pb4f XPS spectra after PbS chemical bath deposition for 85 mins at pH 11 on –COOH terminated SAMs at 22 °C and 45 °C. After deposition the samples were sonicated in deionized water for 2 mins. The colored lines show the fit to the experimental data.

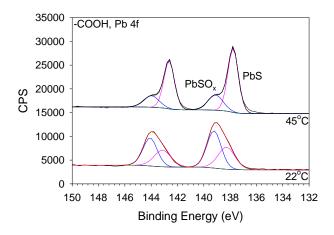


Figure S15. High resolution Pb4f XPS spectra after PbS chemical bath deposition for 85 mins at pH 11 under anaerobic conditions (ie. in a glovebox) on –COOH terminated SAMs at 22 °C and 45 °C. After deposition the samples were sonicated in deionized water for 2 mins. Data obtained using a PHI VersaProbe II, and the colored lines show the fit to the experimental data.

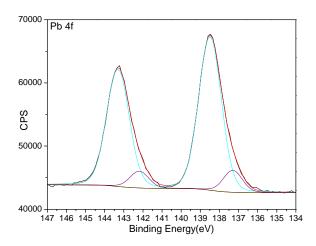


Figure S16. High resolution Pb 4f XPS spectra after PbS chemical bath deposition for 85 mins at 45 °C and pH 11 on –COOH terminated SAMs. Deposition performed under unseeded conditions. The colored lines show the fit to the experimental data.

3.2 PbS Deposition on -CH₃ and -OH Terminated SAMs

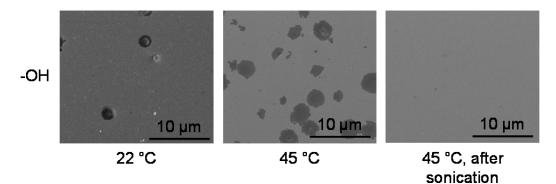


Figure S17. SEM images after PbS chemical bath deposition for 85 mins at pH 11 on –OH terminated SAMs at 22 °C and 45 °C. Also shown is an SEM image of the film after deposition at 45 °C and sonication in deionized water for 2 mins.

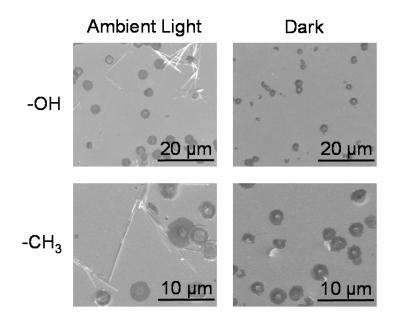


Figure S18. SEM images after PbS chemical bath deposition for 85 mins at pH 11 and 45 $^{\circ}$ C on –OH and –CH₃ terminated SAMs. Depositions were either performed under ambient light or in the dark. Please note that the scale bars in these images are different.

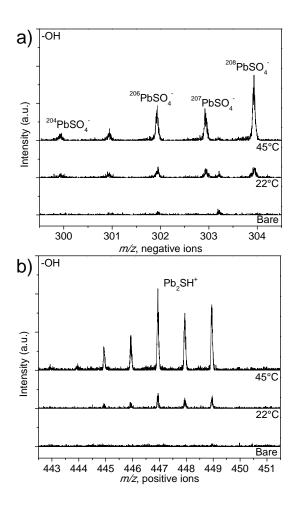


Figure S19. High resolution TOF SIMS spectra centered at a) m/z 302 and b) m/z 447 after PbS chemical bath deposition for 85 mins at pH 11 on –OH terminated SAMs at 22 °C and 45 °C. Also shown for reference is the SIMS spectrum of the bare –OH terminated SAM.

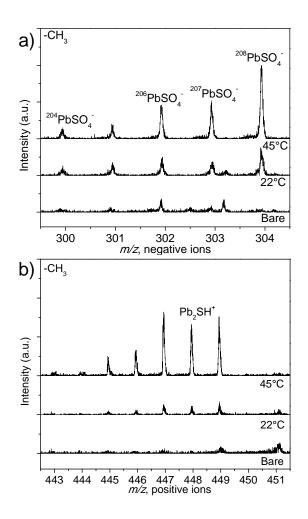


Figure S20. High resolution TOF SIMS spectra centered at a) m/z 302 and b) m/z 447 after PbS chemical bath deposition for 85 mins at pH 11 on $-CH_3$ terminated SAMs at 22 °C and 45 °C. Also shown for reference is the SIMS spectrum of the bare $-CH_3$ terminated SAM.

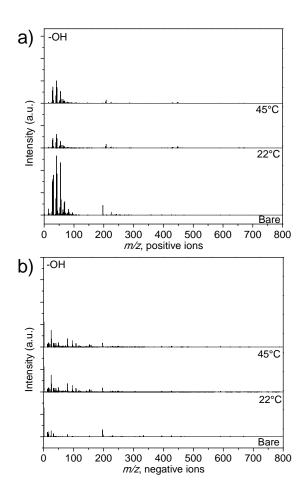


Figure S21. Positive and negative TOF SIMS spectra m/z 0-800 after PbS chemical bath deposition for 85 mins at pH 11 on –OH terminated SAMs at 22 °C and 45 °C prior to sonication. Also shown are the spectra of the bare monolayer.

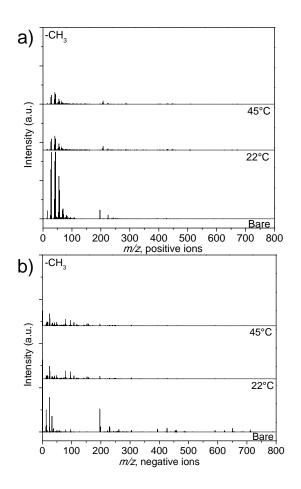


Figure S22. Positive and negative TOF SIMS spectra m/z 0-800 after PbS chemical bath deposition for 85 mins at pH 11 on $-CH_3$ terminated SAMs at 22 °C and 45 °C prior to sonication. Also shown are the spectra of the bare monolayer.

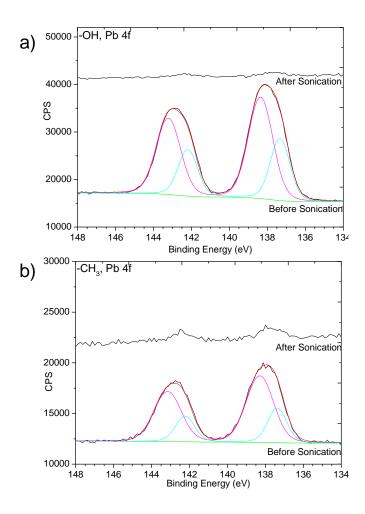


Figure S23. High resolution Pb4f XPS spectra after PbS chemical bath deposition for 85 mins at 45 °C and pH 11 on (a) –OH and (b) –CH₃ terminated SAMs before and after sonication in deionized water for 2 mins. The colored lines show the fit to the experimental data.

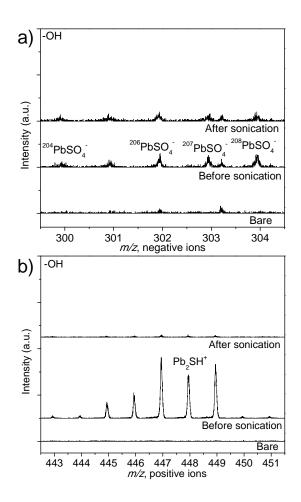


Figure S24. High resolution TOF SIMS spectra centered at a) m/z 302 and b) m/z 447 after PbS chemical bath deposition for 85 mins at pH 11 and 22 °C on –OH terminated SAMs before and after sonication in deionized water for 2 mins. Also shown for reference is the SIMS spectrum of the bare –OH terminated SAM.

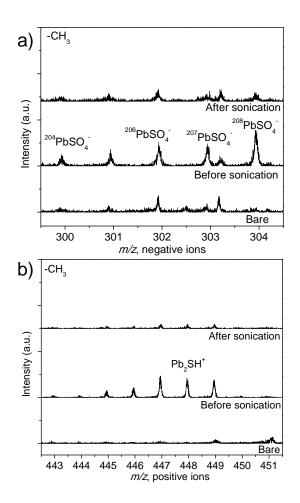


Figure S25. High resolution TOF SIMS spectra centered at a) m/z 302 and b) m/z 447 after PbS chemical bath deposition for 85 mins at pH 11 and 22 °C on $-CH_3$ terminated SAMs before and after sonication in deionized water for 2 mins. Also shown for reference is the SIMS spectrum of the bare $-CH_3$ terminated SAM.

3.4 Towards Pure Ion-by-Ion Growth of PbS

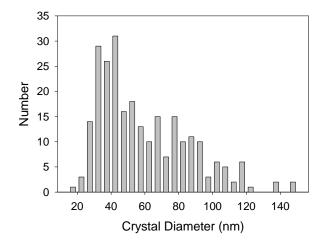


Figure S26. Size distribution of nanocrystallites after PbS chemical bath deposition at pH 11 and 45 °C for 85 mins on –COOH terminated SAM. The sample was sonicated during the deposition.

The size (diameter) distribution of the crystallites was measured from SEM images. The diameter of 256 crystals was measured from two different areas on the sample. The results reported are the average and standard deviation of these measurements

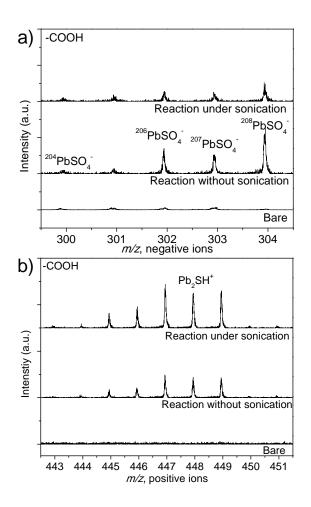


Figure S27. High resolution TOF SIMS spectra centered at a) m/z 302 and b) m/z 447 after PbS chemical bath deposition for 85 mins at 45 °C and pH 11 on –COOH terminated SAM. Depositions performed while the plating bath and substrate was sonicated ("reaction under sonication") and under our normal reaction conditions ("Reaction without sonication"). Also shown is the spectrum of the bare monolayer.

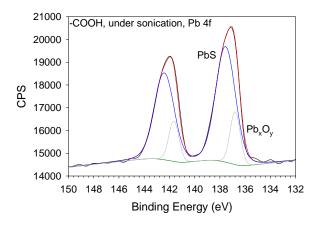


Figure S28. High resolution Pb4f XPS spectra after PbS chemical bath deposition for 85 min for 25 min at 45 °C and pH 11 on –COOH terminated SAM. Deposition performed while the substrate was sonicated in the plating bath. After deposition the sample was sonicated in deionized water for 2 min. The colored lines show the fit to the experimental data.

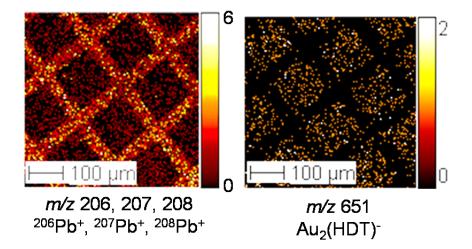


Figure S29. TOF SIMS images after PbS chemical bath deposition for 25 min at 45 °C and pH 11 on a patterned $-CH_3/-OH$ terminated SAM. The TOF SIMS images are centered at m/z 206,207,209 (Pb⁺) and m/z 651 (Au₂(HDT)⁻; HDT = -S(CH₂)₁₅CH₃), which is a characteristic ion of $-CH_3$ terminated SAMs. PbS only deposits only on the -COOH terminated SAM areas ("bar" areas) while no PbS is deposited on the $-CH_3$ terminated SAM ("square" areas). TOF SIMS images: area of analysis: 500 x 500 μ m², 128 x 128 pixels. The TOF SIMS image is shown using a heat scale.