Supporting Information

Solid-Phase Colorimetric Sensor Based on Gold Nanoparticle-Loaded Polymer Brushes: Lead Detection as a Case Study

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Figure S1. (A) XPS spectra of as prepared 1 h-POEGMA, (B) ellipsometric POEGMA thickness variations with respect to synthesis time.

Figure S2. (A) Size distribution of small-diameter AuNPs used in this work as measured via dynamic light scattering. The mean size is determined to be 4.2 nm. Inset show a TEM image of the AuNP sample. (B) UV-vis spectra of as-prepared solution of AuNP with an absorbance peak at 517 nm.
Figure S3. UV-vis spectra from a set of 30 samples of as-prepared (A) APTS-treated, (B) 1 h-POEGMA, (C) 3 h-POEGMA and (D) 6 h-POEGMA obtained from 3 separate synthesis batches of 10 samples each.
Figure S4. UV-vis spectra of as-prepared samples, after thiosulfate functionalization and after 2ME addition of (A) APTS-treated, (B) 1 h-POEGMA, (C) 3 h-POEGMA and (D) 6 h-POEGMA.
Figure S5. UV-vis spectra from a set of 30 samples of (A) APTS-treated, (B) 1 h-POEGMA, (C) 3 h-POEGMA and (D) 6 h-POEGMA obtained from 3 separate synthesis batches of 10 samples each, after thiosulfate functionalization.

Figure S6. Solution phase responses with respect to Pb^{2+} concentrations ranging from 1 pM to 1 µM. Error bars represent standard deviation (n=3).
Figure S7. UV-vis spectra of retrieved 1.0 mM 2ME solution (pH 10) after immersion with (A) as-prepared AuNP-loaded 1 h-POEGMA substrate and (B) thiosulfate-protected AuNP-loaded 1 h-POEGMA.

To confirm the ability of AuNPs to be released from the polymer brush matrix, we performed an investigation with AuNPs within the POEGMA which are not protected with thiosulfate. Upon addition of blank solution of 2ME, the sample is stripped and the release of AuNPs became noticeable when the solution acquired a mild tinge of pink at the region above the sample surface. This coloration eventually diffused evenly throughout the solution. Here the thiol group of 2ME strongly displaces the multidentate interaction between the EG groups of the brush and the gold surface allowing the release of the AuNPs. When the solution is retrieved and checked for its UV spectra, an absorbance peak around 520 nm is clearly present. In contrast, for nanoparticles which have been functionalized with thiosulfate, no coloration developed in the solution. The UV spectra from the solution also did not indicate any detectable absorbance peak, suggesting minimal release of AuNPs from the brush, if any.
Figure S8. X-ray photoelectron spectroscopy (XPS) scans between Binding energies of 126-146 eV from 1-h-POEGMA substrates after detection of (A) 100 nM and (B) 1 µM Pb\(^{2+}\). Raw signal was baselined and curve-fitted using Origin Pro 8 software. A weak Pb4f peak appeared in (B) on top of a common broad peak in both (A) and (B), which is possibly a Si plasmon loss peak. X-ray photoelectron spectroscopy (XPS) scans between Binding energies of 78-96 eV from 1-h-POEGMA substrates after detection of (A) 100 nM and (B) 1 µM Pb\(^{2+}\).

To confirm the formation of Au-Pb alloy during detection and that such formation leads to the release of the nanoparticles from the polymer brush matrix, we have performed X-ray photoelectron spectroscopy (XPS) and found that after detection of 1 µM of Pb\(^{2+}\), a faint Pb4f peak appears. However, when the concentration is reduced to 100 nM, no Pb4f peak was observed. At the same time, as expected, Au4f peaks showed lower intensity after detection of 1 µM Pb\(^{2+}\) compared to 100 nM Pb\(^{2+}\) due to the higher degree of nanoparticle release from the polymer brush matrix. Taking these evidences together, we can conclude that the formation of Au-Pb alloy is responsible for the release of nanoparticles from the polymer.
brush. Since nanoparticles at the top of the brush are easier to be removed than those underneath, at 1 µM Pb\(^{2+}\), most of the nanoparticles at the top with Au-Pb alloy on their surfaces will already be released, leaving behind those underneath. For the case of the latter, they have Pb\(^{2+}\) adsorbed on their surface but with no formation of Au-Pb alloy yet, hence they still remain within the brush. This allows us to observe the Pb4f peak. In contrast, at 100 nM Pb\(^{2+}\), there is just enough Pb\(^{2+}\) to form Au-Pb alloy on nanoparticles which are at the top of the brush. Hence, these particles have already been released leaving behind only AuNPs without with no Pb\(^{2+}\) adsorbed; therefore no Pb4f peak could be observed.

Figure S9. Responses to interfering ions at 100 µM in the absence of 1 µM Pb\(^{2+}\). Error bars represent standard deviation (n=3).
Figure S10. (A) N 1s XPS spectra obtained from APTS-AuNP substrates after detection of 1 µM lead ions in serum (red trace) and water (black trace). (B) N 1s XPS spectra obtained from 1 h-POEGMA-AuNP substrates after detection of 1 µM lead ions in serum (red trace) and water (black trace). Compared to APTS-treated substrates, the N 1s spectra (used to imply the presence of amino acids on the surface) from 1 h-POEGMA substrates after lead detection from human serum revealed a significantly reduced peak implying the ability of POEGMA to deny non-specific adsorption of proteins.
Figure S11. (A) Plot of absorbance versus reaction time obtained from 1 h-POEGMA samples during immersion in 1.0 mM thiosulfate (a), 1.0 mM 2ME (b) and 1.0 mM 2ME with 100 µM Pb$^{2+}$ (c). UV-vis spectra showing the drop in absorbance at every 2 minute interval during immersion of the substrates in (B) thiosulfate, (C) blank 2ME and (D) 100 µM Pb$^{2+}$. 