

Supplementary Information for

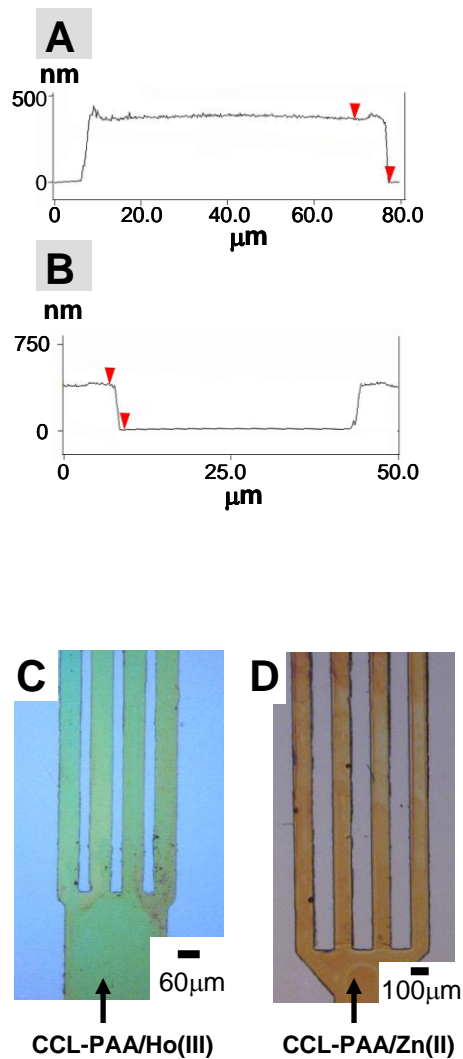
Patterning of Polyacrylic Acid by Ionic Exchange Reactions in Microfluidic Channels

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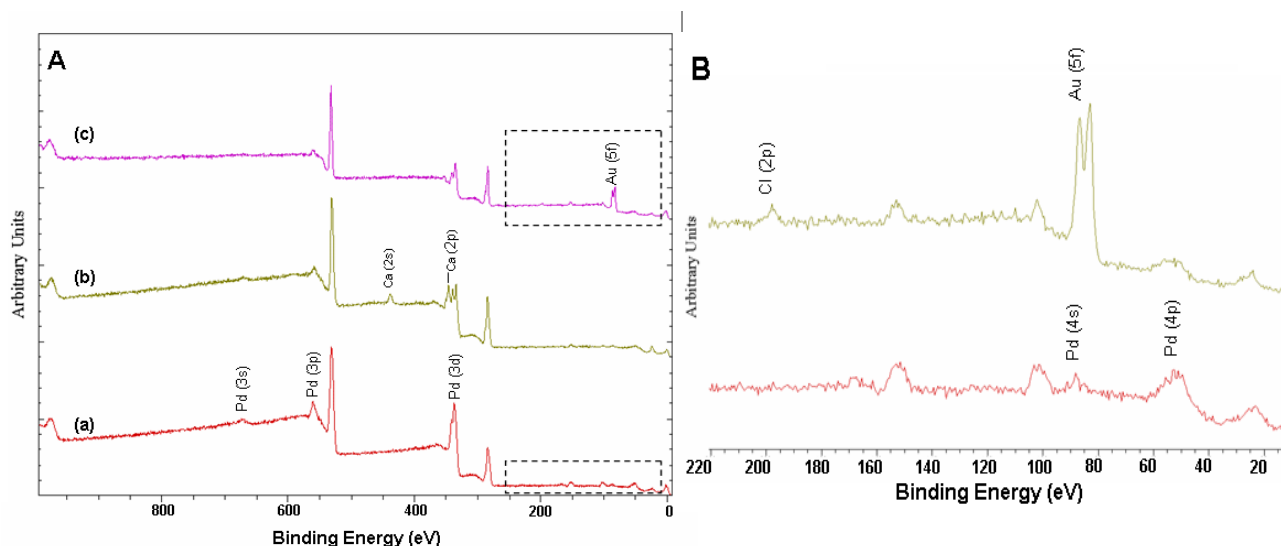
Figure S1



A,B) AFM profiles of the cross-section of the PAA features (from Figure 2A) showing **(A)** a PAA plateau and **(B)** a valley between PAA regions. In both cases, the step height is ~355 nm.

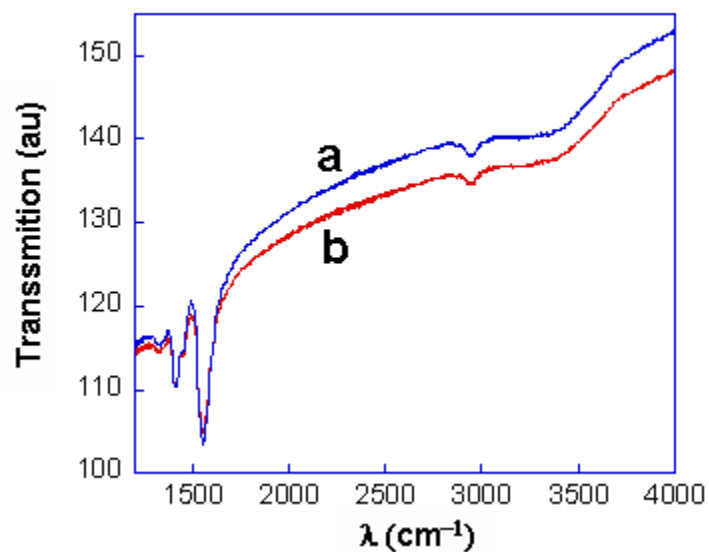
C,D) Optical images of a patterned PAA structure cross-linked by **(C)** 1M Ho(NO₃)₃·5H₂O in methanol/water (v/v, 70/30) solution and **(D)** 1M ZnAc₂ in H₂O. The channel dimensions are **(C)** 60 μm wide spaced by 30 μm and **(D)** 100 μm wide spaced by 100 μm.

Figure S2



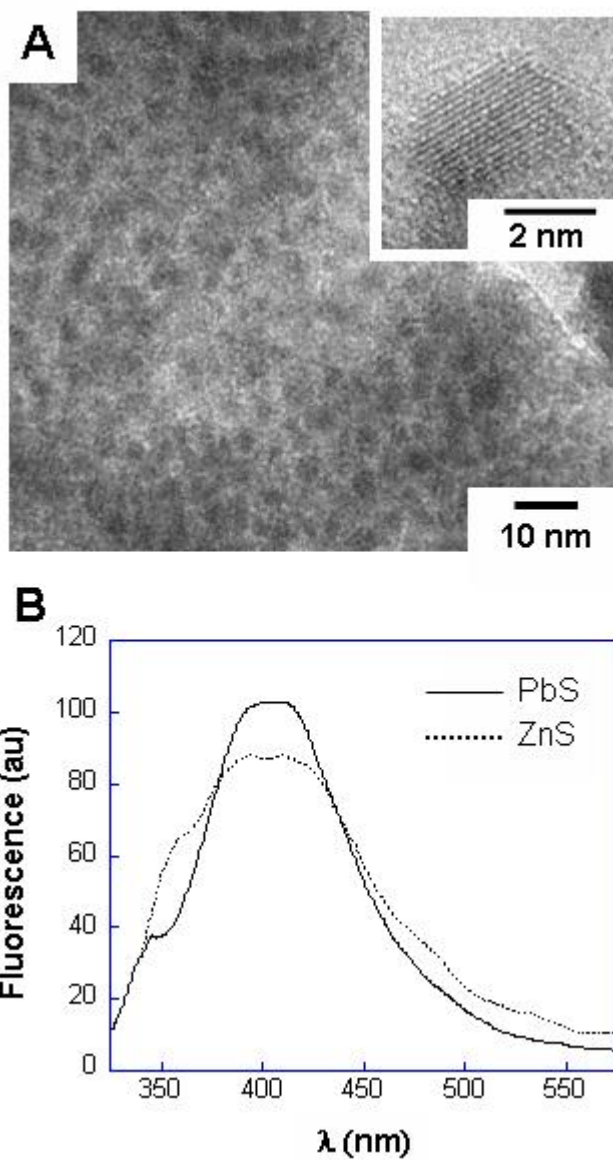
A) XPS data for the surface of PAA films (a) cross-linked with PdSO₄ in methanol/water, (b) exposed to a solution of BDC to reduce the CCL-PAA/Pd(II) film in the presence of CaCl₂ (1M) for 2 minutes, and (c) subsequently treated with 0.5 M NaAuCl_{4(aq)} for 30 min. **B)** Expansion of the marked region in (A). Peaks at all the characteristic orbital energies of palladium were observed in addition to those of oxygen and carbon from PAA. The XPS data were referenced to the carbon peak at 284 eV. After reduction of gold, intense peaks corresponding to Au 5f orbitals appeared, and the intensity of the Pd peaks decreased. A small amount of Cl was observed on the surface, most likely a result of the NaAuCl₄ salt.

Figure S3



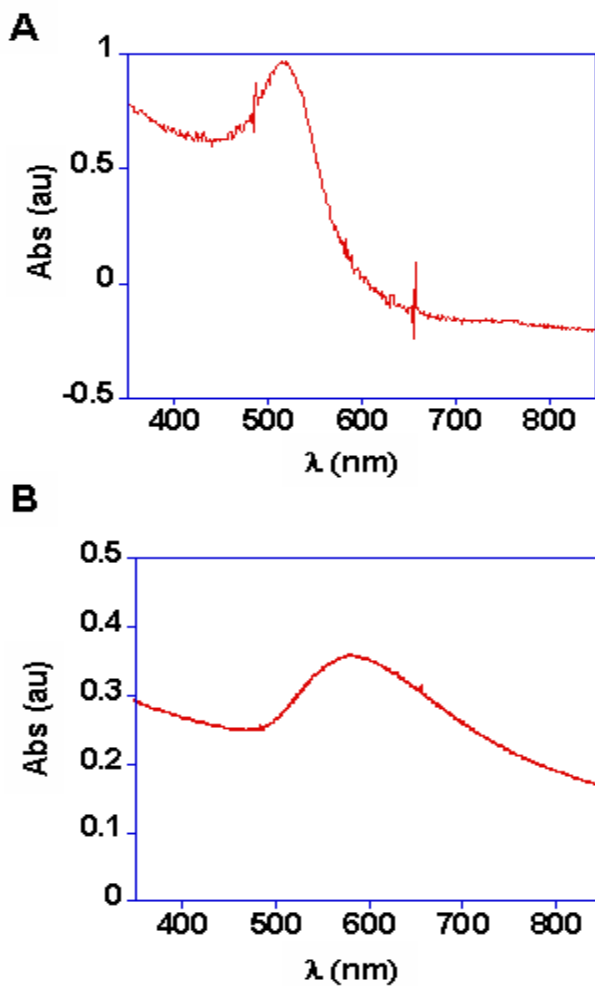
FT-IR spectra of a cross-linked PAA film by La(III) (a) before and (b) after exposure of the film to a reducing solution containing BDC. The location and intensity of the peak from the carbonyl functional group at $\sim 1550 \text{ cm}^{-1}$ did not change between the two spectra.

Figure S4



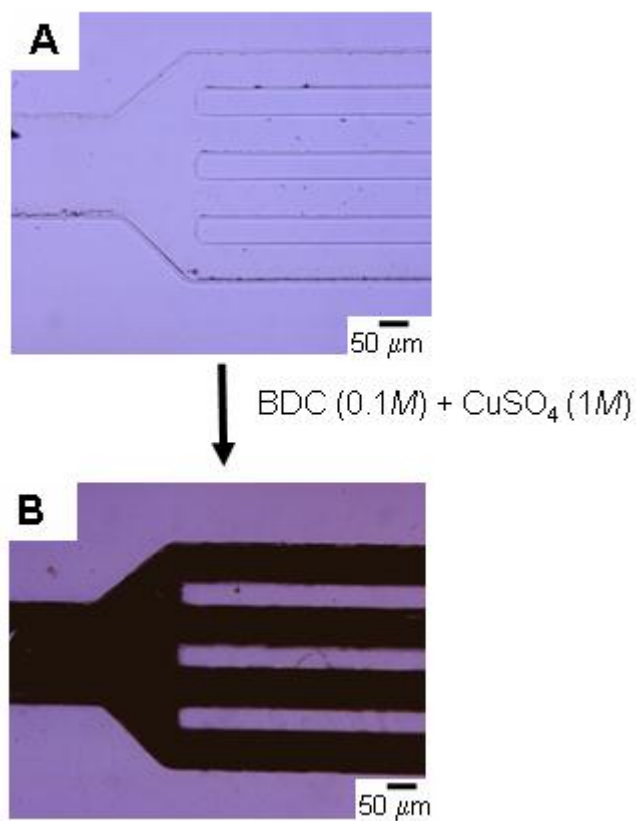
A) A top-view of a CCL-PAA/Ca(II) film containing ZnS nanoparticles. *Inset:* Higher magnification of the film showing one particle with a diameter of ~ 3 nm. **B)** Fluorescence spectra from the semiconductor particles, ZnS and PbS, in solution after dissolution of the PAA film with a solution of 1 M NaOH.

Figure S5



UV-Vis absorption spectra of cross-linked PAA films containing gold nanoparticles embedded within the polymer. **A)** A PAA film cross-linked with PdSO₄ in methanol/water for 20 minutes and subsequently exposed to an aqueous solution of 0.5 M NaAuCl₄ for 30 min. The absorbance of the Au particles had $\lambda_{\text{max}} \sim 520$ nm; this peak is a characteristic absorbance for gold nanoparticles with a diameter ~ 15 nm. **B)** A CCL-PAA/Pd(II) cross-linked PAA film prepared in methanol, reduced with BDC in the presence of CaCl₂ (1M) for 2 min, and subsequently exposed to an aqueous solution of 0.5M NaAuCl₄ for 30 min. The absorbance of the Au particles was red-shifted ($\lambda_{\text{max}} \sim 580$ nm) and broadened with respect to the peak in (A).

Figure S6



Optical images of PAA lines on a glass substrate after cross-linking with a (A) saturated PdSO₄ solution in methanol /water and (B) subsequently reducing the Pd(II) with an aqueous solution containing 0.1 M BDC and 1 M CuSO₄. If the reduction continued for more than 5 minutes, the patterned structure detached from the substrate.