

Patterning of Poly(acrylic acid) by Ionic Exchange Reactions in Microfluidic Channels**

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Here, we describe the in-plane patterning of thin films of poly(acrylic acid) (PAA) within microfluidic channels by crosslinking with metal cations. The patterned polymer and embedded metal ions (Pb^{II} , Ba^{II} , Zn^{II} , Pd^{II} , Cu^{II} , La^{III} , or Ho^{III}) are a platform for the rapid “on-chip” growth of patterned metallic and semiconductor nanoparticles; these particles, in turn, serve as catalysts for electroless deposition of a metal film. The patterned, crosslinked polymer serves as both a reactant and a matrix for subsequent chemistry; nanoparticles grow in patterned regions defined by the crosslinked PAA in seconds, rather than self-assembling over hours on a preformed patterned surface.

We patterned the PAA film with a solution of metal cations in methanol/water flowing through a poly(dimethylsiloxane) (PDMS) microfluidic channel that was in contact with the film of PAA. This solution crosslinked the polymer and thus reduced its solubility in water. After removing the PDMS stamp and rinsing the substrate with methanol, water was used to dissolve those regions of the PAA film that were not crosslinked; this process generated a topologically patterned surface comprising features of PAA with lateral dimensions as small as 500 nm and vertical dimensions of ca. 350–500 nm. Reductants (e.g., BDC: borane dimethylamine complex) and other reagents (e.g., Na_2S) converted appropriate crosslinking cations (e.g., Pd^{II} or Zn^{II}) to metallic or semiconducting nanoparticles, respectively, throughout the PAA matrix. All cation conversion was completed within a microfluidic channel, permitting several types of nanoparticles to be patterned simultaneously on the same “chip”.

Nanoparticles patterned^[1,2] on the sub-micrometer scale are useful as nucleation sites for the growth of patterned nanostructures.^[3,4] Our approach for crosslinking the polymer within microfluidic channels enables further reactions to be done using a combinatorial strategy: we can in principle simultaneously introduce a set of crosslinking solutions of different multivalent metal cations into the channels in the PDMS array and thereby form a pattern of lines (or any desired shape), each with a different functionality. In addition, soft lithography allows rapid fabrication of a wide array of channel geometries.^[5]

Thin polymer films patterned on glass, semiconductor, and plastic substrates are useful in microelectronics, optics, catalysis, and medical diagnostics.^[6] Conventional^[7] and more specialized (e.g., topographically directed and near-field contact mode)^[8,9] photolithography techniques for patterning polymers are limited because they are not compatible with a large number of heat- and light-sensitive polymers and substrates. Electron-beam writing^[10] and laser ablation^[11,12] are capable of patterning a wider range of materials than photolithography but are inherently nonparallel and slow. Several successful techniques, such as solvent-assisted micromolding (SAMIM)^[13,14] and micromolding in capillaries (MIMIC),^[15–17] both based on soft lithography, can pattern a diverse set of organic films and polymers into arbitrary geometries. Nanoimprint lithography,^[18–20] step and flash lithography,^[21] and capillary force lithography^[22] fabricate features in a polymer substrate defined from a topographically patterned stamp (typically PDMS).

PAA is an organic polymer with carboxylate functionalities that can be crosslinked by binding metallic cations.^[23,24] PAA has several desirable features: i) Crosslinked PAA structures are insoluble in both organic solvents and water (at pH 7), so it is a robust polymer for biological applications, such as the controlled release of drugs *in vivo*^[25,26] and cell patterning on hydrophobic surfaces.^[27] ii) The crosslinking of PAA is a reversible process; the crosslinked polymer again becomes soluble when it is exposed to metal chelating agents (e.g., ethylenediaminetetraacetic acid: EDTA) or non-crosslinking ionic solutions (e.g., 1 M NaCl). This reversibility makes PAA an ideal sacrificial layer for applications such as surface micromachining.^[28] iii) The metallic cations bound to PAA can either be reduced to form metallic colloids or precipitate as semiconducting colloids.^[29,30]

We patterned PAA within microfluidic channels using metal-cation solutions. Following the procedure established by Linder et al. (Fig. 1),^[28] we spin-coated a 3.5 % (w/v) aqueous

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[**] This research was supported by an NIH award (NIH GM065364) and used the shared Resource Facilities supported by the National Science Foundation under NSEC (PHY-0117795) and MRSEC (DMR-0213805) awards. M. N. acknowledges support from an NIH fellowship (T32-GM07598). R. P.-C. gratefully acknowledges the Generalitat de Catalunya (DURSI) for support in the form of a post-doctoral fellowship. E. A. W. thanks the Petroleum Research Fund of the American Chemical Society for a fellowship (PRF # 43083-AEF). Supporting Information is available online from Wiley InterScience or from the author.

solution (pH 2.5) of PAA (weight-average molecular weight (M_w) ca. 50 000 g mol^{-1}) onto either a silicon wafer or a glass slide pretreated with oxygen plasma, and heated the film for 15 min at 150 °C. We spun a second layer of 3.5% PAA sodium salt (pH 7.2) onto the first layer of PAA and heated it for 2 min at 150 °C. The first layer of PAA (pH 2.5) increased the adhesion strength of the PAA film to the substrate. The total thickness of the PAA film was ca. 350–500 nm (determined by atomic force microscopy (AFM), see Supporting Information Fig. S1A and B). At pH 7.2, the solution of PAA contains deprotonated carboxylate functionalities (the pK_a of PAA is 5–6, depending on the polymer concentration and the ionic strength).^[31]

We plasma-oxidized an array of microfluidic channels molded in PDMS and brought this stamp into conformal contact with the PAA film. This contact was reversible: the PDMS stamp could be removed from the surface easily at any point during the experiment. External pressure was applied between the top of the PDMS and the underlying substrate

with a vise and prevented leakage from the channels during the patterning process. We placed a drop of one of the metal-cation solutions, either $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 M), BaCl_2 (1 M), $\text{Pb}(\text{Ac})_2$ (Ac: acetate; 1 M), $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1 M), PdSO_4 (saturated) in methanol/water (70:30, v/v), or $\text{Zn}(\text{Ac})_2$ in water (ca. pH 7), at one end of the channel; the solution was drawn through the channels by capillarity without applying external pressure. The ionic solutions crosslinked the underlying PAA film in less than five minutes. The methanol/water mixture dissolved most metal cations with the choice of an appropriate anion. The maximum solubility of PAA in the methanol/water mixture is less than that in water alone, so we could limit the crosslinking to the regions of PAA directly under the microfluidic channel. Typically, when we used water alone as the solvent, we observed penetration of metal ions under the PDMS template through the PAA matrix; this “undercutting” resulted in crosslinking of the PAA film beyond the confines of the channel geometry. The one exception where we were able to crosslink the PAA film with high pattern fidelity was with $\text{Zn}(\text{Ac})_2$ in an aqueous solvent ($\text{Zn}(\text{Ac})_2$ is insoluble in a water/methanol mixture, see Fig. S1D).

We subsequently baked the PDMS/PAA at 90 °C until the sample was dry, removed the PDMS, and rinsed the PAA film with methanol to remove excess salts; these steps did not dissolve the PAA film. Rinsing the PAA film with 18 M Ω water (pH 7.4) dissolved and removed the non-crosslinked polymer. Large-area, continuous, patterned structures of cationic cross-linked PAA (CCL-PAA), conforming to the geometry of the microfluidic channels, resulted after removal of the non-crosslinked PAA with water (Fig. 2). We have produced lines of polymer longer than 2.5 cm (Figs. 2A and S1C,D). The roughness of the edge along this long channel is a few micrometers; this resolution is determined by that of the transparency photomask from which the microfluidic channels were replicated (inset in Fig. 2A). The cross section of a PAA feature, as measured by AFM, was flat with a surface roughness (RMS) of 6 nm, and its profile showed a well-defined step (Fig. S1A,B). We have produced curved PAA features (Fig. 2B), and lines as thin as 500 nm (Fig. 2C and D). The resolution of the patterning is currently limited by the resolution of the chrome mask used to fabricate the channels.

We could also etch the patterned CCL-PAA by exposing it to an aqueous solution containing either an excess of non-crosslinking metal cations (NaCl , 1 M) or a metal chelator (EDTA, 10 mM, pH 8.2) for less than 5 min at room temperature. These solutions un-crosslinked the patterned CCL-PAA and allowed the PAA structures to dissolve.

We fabricated and characterized Pd, PbS, and ZnS nanoparticles within the PAA matrix. The reduction of Pd^{II} into metallic colloids (Pd^0) is one example of useful chemistry that can be done with the patterned, crosslinking metal ions: Pd^0 can reduce other precious metal cations that have a higher oxidation potential, for example, Au^{III} , and provides a catalytic surface for other chemical reactions (e.g., the reduction of Cu^{II}). We have prototyped both of these applications. We used two different reducing agents to convert Pd^{II} embedded in the

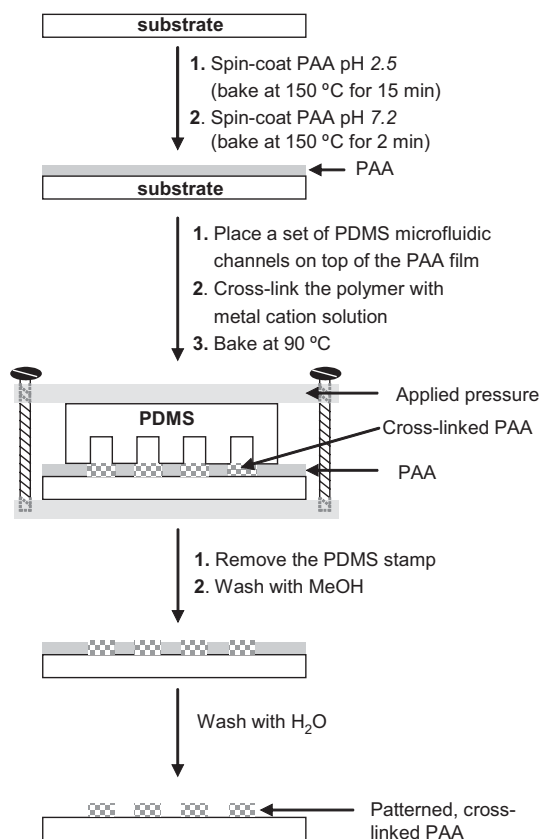


Figure 1. Schematic outline of the procedure used to fabricate patterns in PAA. After spin-coating a thin film of PAA onto a silicon wafer or glass slide, a plasma-oxidized PDMS stamp was placed on the film to define the pattern of the structures. A methanol/water solution of multivalent cations crosslinked the PAA film in the regions beneath the channels. Rinsing the surface with methanol (to remove excess salt), followed by dissolution of the non-crosslinked PAA with water, revealed the patterned PAA.

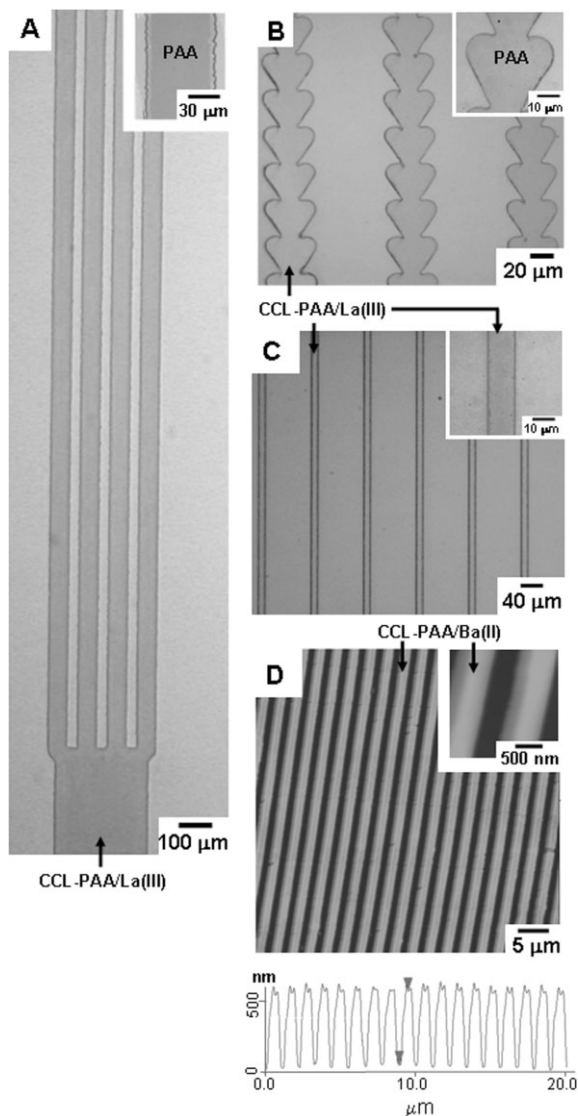


Figure 2. A–C) Optical images showing a patterned PAA structure cross-linked by exposure to 1 M $\text{La}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ in methanol/water (70:30, v/v) for 5 min. The non-crosslinked PAA was then dissolved and removed with water. A) The crosslinked PAA lines, 60 μm wide, spaced by 30 μm , are over 2.5 cm in length. Inset: A higher magnification of a patterned region illustrates that the edge resolution is similar to that of soft lithography using a transparency photomask. B) “Heart-shaped” channels. C) Set of straight channels: the channel width and spacing are 13 μm and 80 μm , respectively. D) AFM image of lines of CCL-PAA/Ba^{II} spaced by ca. 500 nm (top), representing the lower limit we have demonstrated for the resolution of this technique, and a profile of the cross section of the patterned surface over a length of 20 μm (bottom).

PAA matrix to Pd⁰ nanoparticles: methanol, a mild reductant, and a 0.1 M aqueous solution of BDC (in the presence of 1 M CaCl_2 , a replacement cation),^[32] a stronger reductant than methanol. Reduction of the CCL-PAA/Pd^{II} by BDC in a solution without the replacement cation resulted in dissolution of the polymer film. Other cations, such as Zn^{II} or La^{III}, could also serve as replacements for Pd^{II}. We introduced the reductants to the crosslinked PAA in two ways: i) Before removing

the PDMS, we rinsed the channel and CCL-PAA with methanol and then placed a drop of methanol or BDC solution at one end of the channel; the drop was drawn into the channel by capillarity (as occurred with the solutions of metal ions). ii) After removing the PDMS from the support and rinsing with methanol and water, we put a drop of the reductant on top of the patterned polymer. Exposure of the CCL-PAA/Pd^{II} film to the BDC solution for 2 min ensured complete reduction of the palladium cations. The reduction of Pd^{II} by BDC is marked by the evolution of H₂ gas from a side reduction of water (according to the reaction $\text{BH}_3 + \text{H}_2\text{O} \rightarrow \text{B}(\text{OH})_3 + \text{H}_2(\text{g})$). For both methanol and BDC, after reduction, the film appeared darker than the pre-reduction film due to the presence of Pd colloids.^[33] X-ray photoelectron spectroscopy (XPS) measurements confirmed the presence of palladium on the surface of the PAA film (Fig. S2), and a transmission electron microscopy (TEM) image of the cross section of the film showed that the Pd⁰ colloids were distributed throughout the thickness of the entire PAA film (Fig. 3A). Figures 3B and S4A are top-view TEM images of PbS and ZnS nanoparticles, respectively, embedded in the PAA matrix, prepared by reacting the cross-

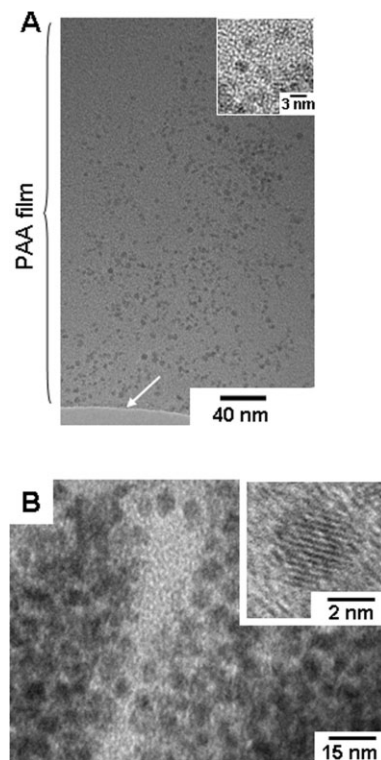


Figure 3. TEM images: A) An 80 nm thick cross section of a CCL-PAA/Ca^{II} film that contains Pd⁰ nanoparticles, after the reduction of Pd^{II} by BDC in the presence of CaCl_2 . Colloids of palladium are observed across the entire polymer matrix; particles are present along the bottom edge of the PAA film (the edge that was originally on the silicon wafer and is indicated by a white arrow) all the way to the top (ca. 350 nm high). Inset: Higher magnification of the film showing that the colloids are ca. 4 nm in diameter. B) Top view of a CCL-PAA/Ca^{II} film containing PbS nanoparticles. Inset: Higher magnification of the film showing one particle with a diameter of ca. 3 nm.

linking cations (Pb^{II} or Zn^{II}) with 10 mM Na_2S solution in the presence of 1 M CaCl_2 for 5 min. In all cases, the nanoparticles were approximately (4 ± 1) nm in diameter.^[23]

We demonstrated “on-chip” chemical reactions with the patterned Pd^0 nanoparticles. After reduction of the Pd^{II} to Pd^0 using either methanol or BDC, we exposed the PAA film containing Pd^0 colloids to a solution of 0.5 M $[\text{NaAuCl}_4]$ for 30 min.^[34] When methanol was used to reduce Pd^{II} to Pd^0 , the PAA film acquired a red color during subsequent reduction of Au^{III} to Au^0 ; when BDC was used to reduce Pd^{II} , the PAA film acquired a blue color during subsequent reduction of Au^{III} to Au^0 . The red color indicated the presence of gold colloids, and the blue color indicated the presence of their aggregates. XPS and UV-vis absorption measurements (see Figs. S2 and S5, respectively) confirmed these assignments. The color of the Au particles was determined by the chemical used to reduce Pd^{II} . We suspect that the use of methanol yielded mainly individual Au nanoparticles because it is a weak reductant of Pd^{II} , and consequently produced Pd^0 nanoparticles (and, subsequently, Au nanoparticles) that were spaced by an average distance large enough to have an absorption spectrum characteristic of individual particles (Fig. S5A). Conversely, since BDC is an excellent reducing agent of Pd^{II} , it yielded a high density of Pd^0 colloids that, upon reduction of Au^{III} , led to aggregated Au nanoparticles (Fig. S5B).

After crosslinking PAA with Pd^{II} within the PDMS microchannels, we injected an aqueous solution containing 0.1 M BDC and 1 M CuSO_4 into the channels that now contained the CCL-PAA/ Pd^{II} film (Fig. 4). This procedure resulted in the reduction of Pd^{II} and Cu^{II} to yield (after rinsing with water) a continuous copper/crosslinked-PAA film with a sheet resistance of ca. $20 \Omega/\square$. Bubbles of H_2 gas evolved as the Cu^{II} was reduced to Cu^0 (Fig. 4B, indicated by arrows); this evolution of gas was enhanced in the presence of a metallic surface (Pd^0 and Cu^0). Upon completion of the reduction, the PAA film was no longer transparent and gas evolution ceased (Fig. 4C). This process of reducing Cu^{II} with BDC in the presence of CCL-PAA/ Pd^{II} can also be accomplished without the PDMS microfluidic system (Fig. S6). In solution, BDC reduces Pd^{II} to Pd^0 more rapidly (ca. 1 s) than it reduces Cu^{II} to Cu^0 (on the order of hours). The reduction potential corresponding to direct reduction of Cu^{II} by Pd^0 is negative ($E^0 = -0.61$ V), implying that this reaction is not spontaneous. We hypothesize that the reduction of Cu^{II} by BDC in the presence of Pd^{II} that we observe here is a catalytic process: the BDC initially reduces the Pd^{II} to Pd^0 , and the presence of Pd^0 catalyzes the reduction of Cu^{II} to Cu^0 by BDC.

In conclusion, we have employed a set of microfluidic channels as a mold to fabricate a patterned substrate for formation of metal and semiconductor nanoparticles, and these particles have been used to pattern the products of several chemical reactions (electroless deposition of a film of copper, reduction of a gold salt to a disordered array of nanoparticles). In this method of patterning PAA, the metal ions that crosslink the polymer, and, therefore, define the pattern, are reduced to

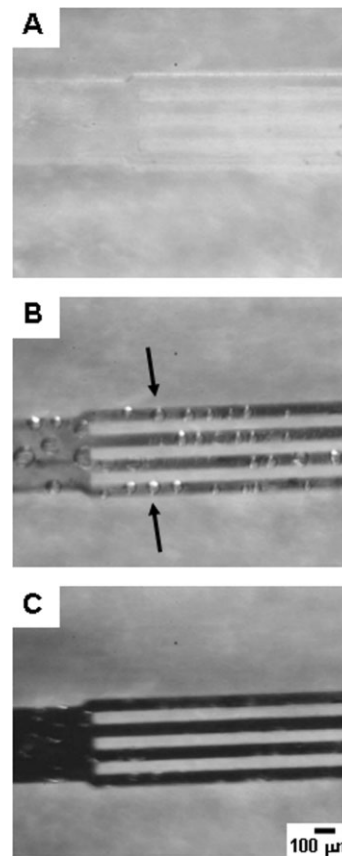


Figure 4. Optical images of patterned lines of CCL-PAA/ Pd^{II} during its reduction by an aqueous solution of BDC (0.1 M) and CuSO_4 (1 M) in a PDMS channel, at times (a) 0, (b) 5, and (c) 20 s. b) Gas bubbles evolved as the Cu^{II} was reduced to Cu^0 by the BDC; this reduction was catalyzed by the Pd^0 nanoparticles. c) Upon completion of the reduction, the PAA film was no longer transparent and gas evolution ceased.

form nanoparticles: the nanoparticles grow in patterns rather than adsorb on a preformed pattern of polymer.

Many ions (Pb^{II} , Ba^{II} , Zn^{II} , Pd^{II} , Cu^{II} , La^{III} , or Ho^{III}) effectively (and reversibly) crosslink PAA within minutes, and the resulting crosslinked polymer gels are not soluble in water or in several organic solvents. The microfluidic channels can template the patterning of both straight and curved features as thin as 500 nm; the resolution of the patterns is currently limited by that of the chrome mask used to fabricate the channels. Some of the embedded metal ions (e.g., Cu^{II} , Pd^{II}) can be reduced to form disordered arrays of nanoparticles embedded in and on the surface of the PAA film. Palladium(0) nanoparticles can then be used for catalyzing the electroless deposition of a Cu film and for reducing Au^{III} to Au^0 nanoparticles.

The procedures described in this work are a means to produce substrates with well-defined, sub-micrometer patterns of crosslinked polymer and metallic nanoparticles without the use of cleanroom facilities.

Experimental

All materials were purchased and used as received, unless otherwise stated.

Patterning PAA within Microfluidic Channels using Metal Cation Solutions: We exposed either a silicon wafer or a glass slide to an oxidizing (air) plasma in a plasma cleaner (ca. 266 Pa, 100 W, Harrick Scientific Model PDC-32G) for 1 min. A solution of PAA (M_w ca. 100 000, Aldrich) diluted to 3.5 % w/v, having a pH of ca. 2.5, was spun-cast (1500 rpm for 15 s) and baked for 15 min at 150 °C on a hot plate. A second layer of PAA (3.5 % w/v), titrated with KOH (Fluka) to a pH of ca. 7.2, was spun (1500 rpm for 15 s) onto the substrate and baked for 2 min at 150 °C. A PDMS microfluidic channel was fabricated using soft lithography techniques [5]. The PDMS microfluidic stamp was plasma-oxidized for 15 s and was held in conformal contact with the PAA film using a vise. A drop of a 1 M or saturated solution of the crosslinking cation (typically in a methanol/water mixture, 70:30 v/v) was drawn into the channels by capillarity and allowed to remain for 5 min. The PDMS/PAA was subsequently baked at 90 °C until the sample was dry, the PDMS was removed, and the PAA film was rinsed with methanol to remove excess salts. Subsequent rinsing of the PAA film with 18 M Ω water (pH 7.4) dissolved and removed the non-crosslinked polymer. All optical images of the PAA structures were obtained on a Leica DMRX microscope; AFM images were collected in tapping mode with a Digital Instruments Dimension 3100 Nanoscope, and analyzed using Nanoscope IV v5.12b18 software.

Formation and Characterization of Nanoparticles: Using appropriate reagents, we converted the crosslinking cations into nanoparticles. A 0.1 M aqueous solution of BDC reduced Pd^{II} to metallic nanoparticles, and a 0.01 M aqueous solution of Na₂S converted both Pb^{II} and Zn^{II} into semiconductive nanoparticles. The size and presence of particles were observed by TEM (JEOL 2100) at 200 kV. The carboxylic functionality on PAA was shown to not be affected by the reduction process using a Fourier transform IR spectrometer (Nexus 670).

The PAA film containing Pd⁰ colloids was exposed to a solution of 0.5 M [NaAuCl₄] for 30 min. The presence of gold colloids was confirmed by UV-vis absorption spectroscopy (Hewlett-Packard 8453) and XPS (Surface Science SSX-100).

Received: August 12, 2006

Revised: September 20, 2006

Published online: November 10, 2006

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- [32] We chose Ca^{II} as the replacement cation because it has a very negative reduction potential ($E^0(\text{Ca}^{II}) = -2.9$ V vs. standard hydrogen electrode (SHE) at 25 °C), and neither the BDC nor the Pd⁰ ($E^0(\text{Pd}^{II}) = 0.95$ V vs. SHE at 25 °C) reduce the Ca^{II} cations.
- [33] The BDC did not reduce the carboxylate functionality of PAA on this time scale, as confirmed by Fourier transform (FT) IR measurements (see Fig. S3).
- [34] If BDC were used to reduced Pd^{II}, the PAA film was thoroughly washed with water to remove all traces of the reductant before exposing the surface to Au^{III}. The presence of BDC prevents Au⁰ colloidal formation within the CCL-PAA matrix, as the BDC more readily reduces Au^{III} and these colloids are subsequently washed away upon rinsing of the film.