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Inkjet Deposition of Layer-by-Layer Assembled Films

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Abstract: Layer-by-layer assembly (LBL) can create advanced composites with exceptional properties unavailable by other means, but the laborious deposition process and multiple dipping cycles hamper their utilization in microtechnologies and electronics. Multiple rinse steps provide both structural control and thermodynamic stability to LBL multilayers, but they significantly limit their practical applications and contribute significantly to the processing time and waste. Here we demonstrate that by employing inkjet technology one can deliver the necessary quantities of LBL components required for film buildup without excess, eliminating the need for repetitive rinsing steps. This feature differentiates this approach from all other recognized LBL modalities. Using a model system of negatively charged gold nanoparticles and positively charged poly(diallyldimethylammonium) chloride, the material stability, nanoscale control over thickness, and particle coverage offered by the inkjet LBL technique are shown to be equal or better than the case of multilayers made with traditional dipping cycles. The opportunity for fast deposition of complex metallic patterns using a simple inkjet printer is also shown. The additive nature of LBL deposition based on the formation of insoluble nanoparticle−polyelectrolyte complexes of various compositions provides an excellent opportunity for versatile, multicomponent, and noncontact patterning for the simple production of stratified patterns that are much needed in advanced devices.

Introduction

Many composite materials produced via layer-by-layer assembly (LBL), the sequential adsorption of monolayers of complementary materials to form layered, insoluble complexes,[1] possess impressive mechanical, electrical, optical, and biological properties desirable in many emerging technologies.[2−6] Such properties would be advantageous in many macro-, meso-, and microscale devices. However, the multiple fluid cycles required for multilayer preparation make this otherwise promising method for the design and fabrication of customized materials time-consuming and often impractical. The abundance of fluids used in the process make it challenging to couple LBL deposition with other processing steps for device fabrication. From this perspective, it is quintessential to investigate other means to produce LBL materials that maintain a similar nanoscale control over structure while accelerating the composite buildup and evolving the technique for better integration with device manufacturing.

Formation of the sequentially adsorbed monolayers is traditionally carried out by alternate dipping of a substrate between two reservoirs of oppositely charged macromolecular compounds, for example, a positively charged polyelectrolyte solution and a negatively charged nanoparticle (NP) dispersion,[7,8] with intermediate rinse steps that remove excess fluid and loosely adsorbed components. The self-limiting nature of the growing film results in a layered pattern transversal to the substrate and a homogeneous assembly of the combined materials, which would otherwise phase separate when directly mixed. Often times the impressive properties of the resulting LBL materials can be attributed to these useful structural features. In large part, these features are due to the presence of rinsing steps believed to prevent the formation of large aggregates with variable composition that destroy the materials' essential qualities, for instance, homogeneity, electrical conductivity, or mechanical strength.

The rinsing steps also appear to be quite important from the perspective of the stability of the multilayers.[9−13] A substantial portion of the Gibbs free energy associated with multilayer formation (and therefore the adhesion strength between the LBL components) originates from the hydration/solvation of ions[9,10] and from entropic contributions originating from the release of low molecular weight counterions into the media[11−13] during the formation of insoluble complexes. Therefore, the rinsing steps appear to be a significant component of LBL assembly

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and necessary from the point of view of basic thermodynamics. Nevertheless, the rinsing steps dramatically limit the practical applications of the LBL technique and add processing time and waste. Modifications to the technology have been developed that accelerate the process with spraying and/or spin coating,[14−18] but rinsing steps are still required for film production and structural control. Therefore, as it has attracted very little attention thus far, it would be very useful and fundamentally interesting to obviate the intermediate rinsing steps. In doing so, one needs to resolve the issue of the excess material left on the surface during dip coating and the low molecular weight inorganic salts released during complex formation.

Encouraged by the development of the dewetting technique where the salt and excess material are removed by the retreating liquid,[19] we investigated alternative approaches to satisfy the hard-to-cheat thermodynamic requirements while still reaching substantial simplification of the process. We hypothesized that if *the proper amount of material necessary for film growth is delivered to the surface without large excess*, constant rinsing after every adsorption step may no longer be necessary. In this way, one can still retain the high level of structural control of the LBL composite, reasonably high homogeneity of the resulting material, and universality of the deposition, i.e. the freedom of mixing and matching the components to gain a unique set of properties. With respect to the release of low molecular weight salts, the actual amount required for multilayer formation is quite small. Since there is substantial diffusion transparency of the LBL films for small ions,[20,21] their removal can potentially be achieved in a final (single) rinse at the end without the destruction of the multilayer assembly. Thermodynamic restrictions on multilayer formation and concerns of fast decomposition of the entire film still likely remain in this process; however if implementation of this idea is possible, it will be exceptionally convenient for a variety of applications and expand the basic understanding of LBL.

In this article we demonstrate the preparation of LBL films using a standard inkjet printer as a practical method to alternately deliver precise amounts of each component for the formation of LBL films without intermediate rinsing. The replacement of the numerous rinsing steps with one final rinse was feasible in this case, indicating that the kinetics of low molecular weight salt removal from the films is fast enough to prevent decomposition of the entire assembly. The technique offers nanoscale control over layer thickness, variable NP coverage of the surface, and compatibility with additive schemes of device manufacturing which set it apart from previous methods of combining inkjet and LBL multilayers.[22−26] In addition, the vast range of materials that can be deposited with this patterning method is currently unavailable with other patterning techniques such as traditional lithography or inkjet printing of conventional materials.[6,27−31] This work leads to the *de facto* new modality of LBL deposition and a convenient method of patterning surfaces with composite materials that is expected to be quite useful for the development of advanced materials and devices.

Previously there have been successful combinations of LBL assembly with inkjet technology;[22−26] however their purpose, scientific rationale, and results are very different. For instance, Rubner et al. dispersed water via inkjet to selectively destroy portions of traditionally deposited LBL multilayers which were pH sensitive.[23] It resulted in a useful patterning method that can be applied to a variety of hydrogen-bonded multilayers but is not suitable for nanocomposites. LBL and inkjet printing were also combined to selectively activate the surface of a multilayer film for electroless metal plating.[25,26] In this case a single polyelectrolyte from the multilayer pair was printed for the purposes of patterning chemical functionalities. More recently, Limem et al. demonstrated that pairs of self-assembling or reactive polymer solutions could be printed to form insoluble gels.[22] This work also described simple patterns but obviated the questions of the accurate control over the multilayer growth that is essential for material design and applications of multilayer films. Multilayer films were also used to modify the print surface for enhanced adhesion and controlled wettability.[24,25]

Experimental Section

Instrumentation. A drop-on-demand Epson R280 photo printer with the capability to print onto CDs was equipped with an external continuous ink system. A CD was modified to allow for placement of various substrates (glass, silicon, plastics), paying attention to the location of the rollers on the printer to prevent contact with the actual sample.

The growth of the film was evaluated by light transmission measurements obtained using an Agilent 8453E UV−visible spectrometer, and thickness measurements were obtained using a single wavelength (532 nm) EP3-SW imaging ellipsometer (Nanofilm Technologie). Four-zone nulling experiments were performed at an angle of incident of 60°, and the ellipsometric parameters psi and delta were modeled with a two-coefficient Cauchy dispersion law ($A = 1.45$, $B = 0.01$). Measurements were taken from five different areas of each sample and averaged together. Scanning electron microscopy images were obtained with an FEI Nova 200 Nanolab.

Materials. High molecular weight poly(diallyldimethylammonium) chloride (PDDA) was purchased from Aldrich and diluted to 0.25 and 0.0025 wt % in deionized water. Citrate stabilized gold nanoparticles (GNPs) with diameters 13 ± 2 and 20 ± 2 nm were synthesized using previously published techniques.[32−34] Briefly,

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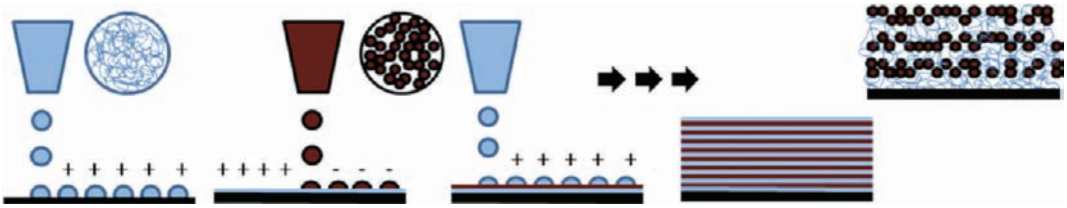

Figure 1. Schematic of multilayer film production by inkjet layer-by-layer assembly.

for 13 ± 2 nm GNPs for example, $HAuCl_4$ in deionized water (0.0005 M, Aldrich) was brought to a boil on a hot plate. Under vigorous stirring sodium citrate in deionized water was added (1% w/w, Aldrich). Vigorous stirring and heat were then added for an additional 15 min. The concentration of the GNPs was increased via centrifugation (Sorvall Legend Mach 1.6R, 10 000 rpm, 30 min), and cellulose membrane dialysis tubing (Sigma) used to remove the excess salt after 2 days in deionized water that was changed every 5−10 h. Finally, the solution was filtered through a 0.22 μm filter to remove aggregates and a final concentration of approximately 2480 GNP per pL of water was obtained.

Process of Inkjet LBL Deposition. The continuous ink system and Epson nozzles were cleaned several times with deionized water, and the yellow and black cartridges were refilled with 0.0025 wt % PDDA and the GNP dispersion respectively. Patterns designed in Adobe Photoshop (CS4 Adobe Systems Inc.) were printed first in yellow (PDDA) for a set number of overprints, x, before being printed in black (GNP) for y overprints onto piranha-washed silicon and glass substrates. The printer was set to operate under the Epson *best photo printer* setting at normal speed with integrated color management and no color adjustment. The bilayer comprising x layers of PDDA followed by y prints of GNP was then repeated z times until the desired film thickness of $(PDDA^x/GNP^y)_z$ was obtained. The substrate was then removed from the printer setup, washed under a stream of deionized water for 1 min, and dried with compressed air.

For traditional dip-coating LBL, a piranha-washed silicon substrate was first soaked in 0.25 wt % PDDA solution for 10 min. It was then rinsed under a stream of deionized water for 1 min and dried with compressed air. The substrate was then soaked in the concentrated GNP dispersion for 10 min before being rinsed and dried again. The four-step sequence was repeated for each of the z bilayers.

Results and Discussion

The deposition and buildup of LBL multilayers with inkjet technology that is explored herein can be taken advantage of in several ways. The mode that is considered here begins with the delivery of an appropriate amount of a positively charged polyelectrolyte ink onto a negatively charged substrate via inkjet deposition (Figure 1). Due to the small volume size of the droplet the solvent is evaporated leaving behind an insoluble film of polymer on the surface and a positive surface charge. A second nozzle is then used to deliver a measured amount of a suspension of negatively charged nanoparticles (NP). The NPs interact with the positively charged polymer forming a nanocomposite. After evaporation of the solvent, the surface charge is then negative again and the process of dispensing each component is repeated until the desired overall thickness is obtained. Several passes of the inkjet printing head dispersing smaller quantities of an LBL component can be used to accurately vary the amount of the deposited polyelectrolyte or NPs. Overall, the idea addresses the significant challenges of LBL mentioned above by delivering *precise amounts of the selected polyelectrolyte and NPs* or any other LBL component to the surface in order to reduce the need for rinsing steps to one final step or only a few intermediate steps to remove the accumulation of low molecular weight salts. This mode of inkjet deposition has the potential to significantly accelerate the preparation of the films while retaining the advantageous layered and homogeneous structures characteristic of LBL deposition. Considering the potential applications of LBL composites in microscale devices, inkjet LBL should also make it possible to pattern surfaces using direct-write methods rather than by different types of etching. Note also that the ability of LBL to make gradient structures[35] will remain and will only require a simple change of ink during buildup of the pattern.

One can compare inkjet LBL as described in Figure 1 to spray LBL deposition, where overcoming the diffusion limitations found in traditional LBL with the direct delivery of material to the surface significantly decreases processing times.[14,36] Films of equivalent quality, adhesion, composition, and morphology to those prepared with traditional LBL techniques have been created with spray LBL despite the fact that the adsorption occurs under nonequilibrium conditions.[14,36] While significantly decreased rinsing times can be implemented with spray LBL, rinsing between depositions is still necessary. Also, while excellent for large-scale coatings, spray LBL lacks control over the size, velocity, and density of the droplet, which are crucial for precise material preparation. Alternatively, drop-on-demand inkjet printing delivers picoliter volumes of ink from a reservoir, ejected through a nozzle with highly controlled size and placement.

Inkjet LBL Assembly of Nanocomposites. Originally demonstrated with the growth of oppositely charged polyelectrolytes,[37] LBL has now been significantly expanded to include alternate chemistries[38−40] and many other materials including colloidal NPs.[41,42] For example, the introduction of gold nanoparticles (GNPs) into organic matrixes using LBL assembly was used to significantly improve the mechanical, optical, and

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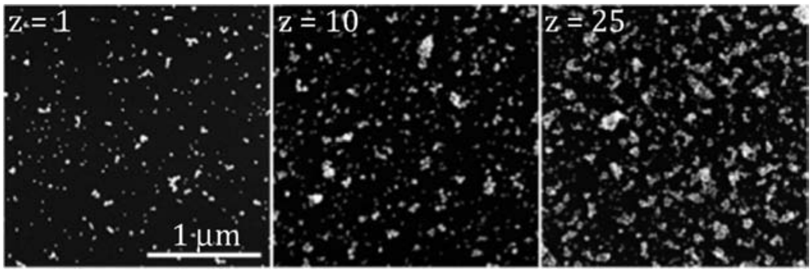

Figure 2. Surface coverage of GNPs in a $(\text{PDDA/GNP})_z$ film produced using standard dip-coating LBL with $z = 1$, 10, and 25 bilayers.

electrical properties of polymeric materials with potential applications in, for example, microelectronic devices, electrochemical sensors, and bioanalysis.[43−45] As spray LBL was successfully used to produce GNP multilayer films,[46] we investigated the capability of the inkjet LBL technique to create multilayered GNP nanocomposites. To test the performance and capabilities of inkjet LBL we chose standard GNPs made with citrate ions as a stabilizer,[34,47,48] with average diameters of 13 ± 2 and 20 ± 2 nm, and a negative surface charge.

The notation $(\text{PDDA}^x/\text{GNP}^y)_z$ will be used throughout the paper to discriminate between different printing programs. To reflect the new possibility of printing of small quantities of one LBL component several times until the desired amount is deposited, *x*, will denote the number of overprints of PDDA jetted on the substrate before *y* overprints of GNP are applied to make up a single bilayer. The entire cycle is then repeated *z* times. When *x* and *y* are absent in the notation, i.e. $(\text{PDDA/GNP})_z$, the multilayers were deposited using standard dip-coating LBL. Typically, greater number of overprints, *x* and *y*, of a solution of lower concentration of the components should result in a more uniform deposition that can overcome the structural disturbances caused by the singularity of each droplet. Ideally, of course, $x = y = 1$ will result in faster film growth with the concentration adjusted to provide monomolecular or monoparticulate coverage of the substrate. One might point out that not all traditionally grown LBL films give uniform dense coatings in the dip cycles and that multiple inkjet passes can definitely improve the film structure. The possibility of using a concentration that results in a higher coverage than that corresponding to monolayer coverall can also be considered as long as the stoichiometry between the components is retained.

For proof of concept we deposited five lines of increasing thickness of $(\text{PDDA}^1/\text{GNP}^1)_z$ onto a silicon wafer by alternating inkjet printing of single print cycles ($x = y = 1$) of the positively charged PDDA and negatively charged GNP for $z = 5$, 10, 15, 20, and 25 bilayers. Despite the patchiness (which is also present in traditional dip-coated LBL films with rinsing, Figure 2), the averaged thickness of the multilayer film grows linearly with the number of depositions, similar to LBL films assembled by dip-coating, spin-coating, or spraying (Figure 3). The average thickness per layer as determined by dividing the average total thickness by the number of bilayers is 1.38 ± 0.34 nm. The thickness per bilayer is less than the diameter of the GNPs due to the GNP surface coverage of the films. As the number of bilayers increases, the content of gold on the surface steadily increases allowing for the average thickness to rise (Figure 3). Notably, the printed multilayers demonstrate denser and more uniform GNP coverage compared to films produced using traditional dip-coating LBL (Figure 2). Note that one can adjust the surface density of NPs in dipped LBL films to reach complete and uniform coverage by different means; however, we did not optimize the conditions of the traditional LBL or the inkjet modality in order to investigate the use of relatively standard conditions with direct use of the as-made GNPs. This is a clear demonstration of the advantageous performance characteristics of inkjet LBL.

Additionally, when considering the case of simple $(\text{PDDA/GNP})_z$ composite films deposited on substrates with a relatively small area (4 cm^2), targeted here as a base for elements of potential everyday devices produced by LBL, one can find a significant improvement in production time with the use of inkjet LBL as compared to using traditional dip-coating LBL (approximately 7 times faster when estimated bilayer deposition times of 4 min for inkjet LBL and 28 min for dip coating are considered). Processing times should be significantly enhanced with advanced printing systems and automation. When subsequent patterning of traditional LBL films is considered, which will need to include other steps, such as photoresist deposition, masking, UV exposure, photoresist removal, etc., improvements in production times with the use of inkjet LBL are even more radical.

The GNP coverage of the inkjet LBL films can be improved further by increasing the number of prints of gold delivered per bilayer. To investigate the range of surface coverage available with the technique, a single layer of 0.25 wt % PDDA was applied to a silicon substrate using dip-coating LBL before six lines of width 318 μm in Adobe Photoshop were printed onto the substrate. The number of prints of gold per line was increased over the following values: $y = 1$, 10, 25, 50, and 75. The washed and dried $(\text{PDDA/GNP}^y)_1$ lines were imaged at different length scales (Figure 4). Comparative surface coverage of GNPs with traditional LBL can be achieved after 1 print (Figure 2, $z = 1$ and Figure 4, $y = 1$). With a greater number of overprints, the GNP coverage gradually increased reaching a complete multi-NP thick layer at about $y = 50$. A further increase in overprints did not strongly affect the layer morphology. The distribution of NPs in the printed layer that was observed without any special effort was quite uniform, which is oftentimes not the case for many inkjet patterned surfaces due to the fairly large droplet size and "coffee ring" effect during drying.[49−51] The concentration of the GNP dispersion can be altered to adjust the coverage and the number of prints needed to obtain the desired GNP coverage and potential thickness of the NP film.

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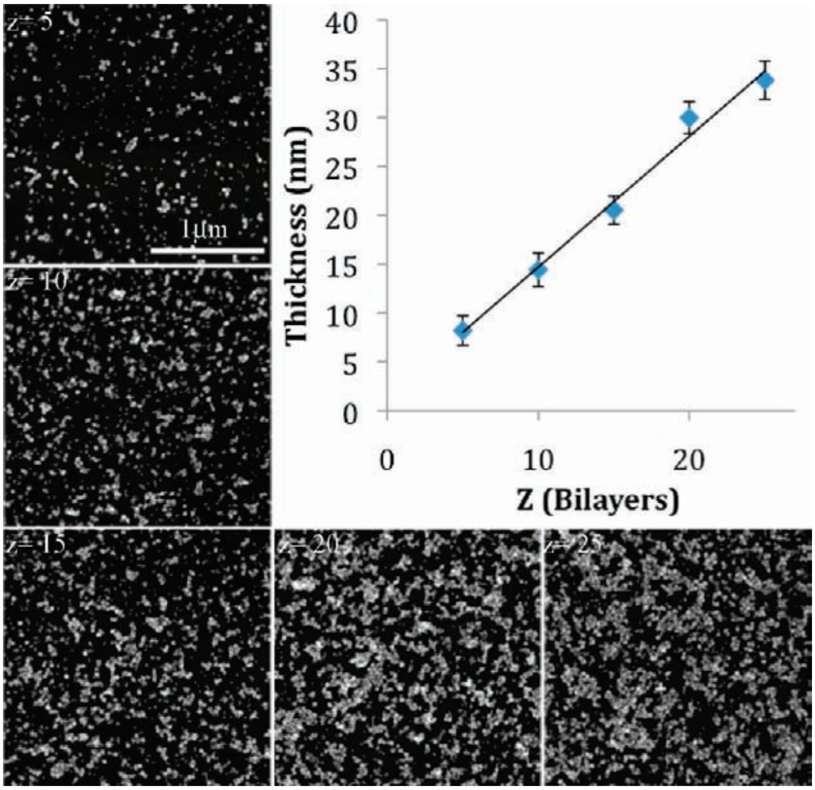

Figure 3. Increasing thickness of (PDDA^1/GNP^1)$_z$ and SEM images of GNP coverage after deposition of *z* bilayers by inkjet LBL.

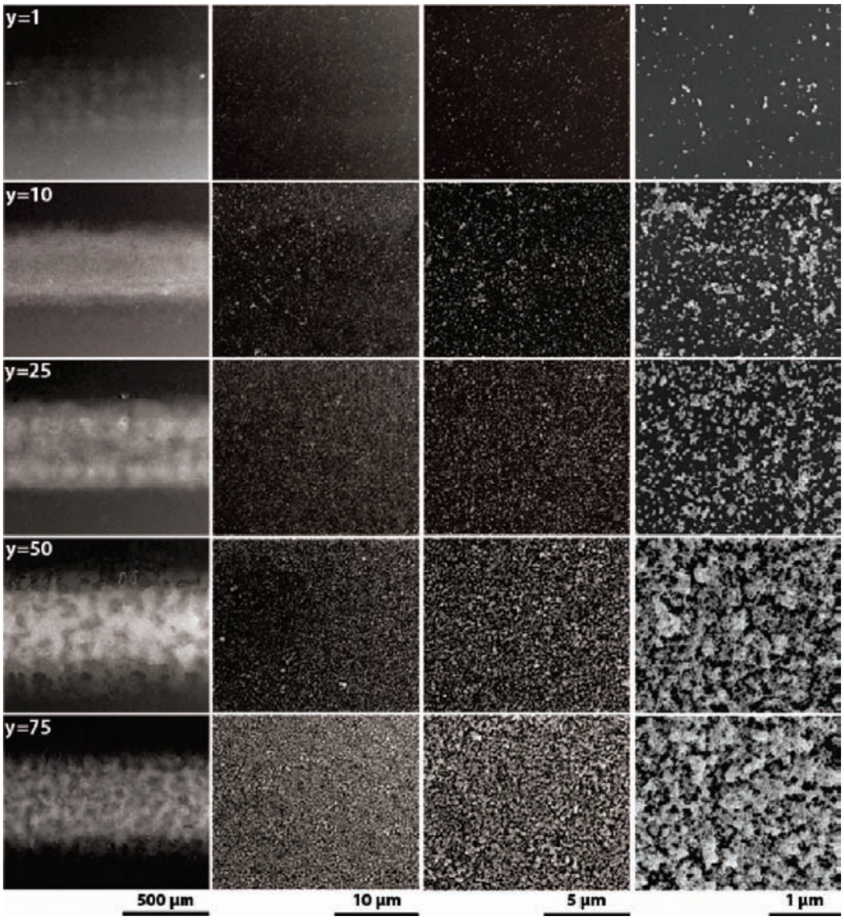

Figure 4. SEM images of a single bilayer of (PDDA/GNP^y)$_1$ LBL films with $y = 1$, 10, 25, 50, and 75 inkjet prints of gold.

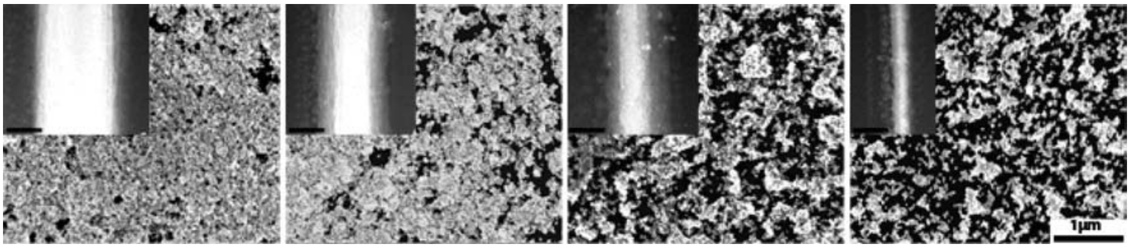

Figure 5. SEM images of inkjet printed $(PDDA^{3}/GNP^{75})_1$ lines of decreasing computer designed widths from left to right of 425, 283, 168, and 66 μm. (Scale bar of inset images = 250 μm.)

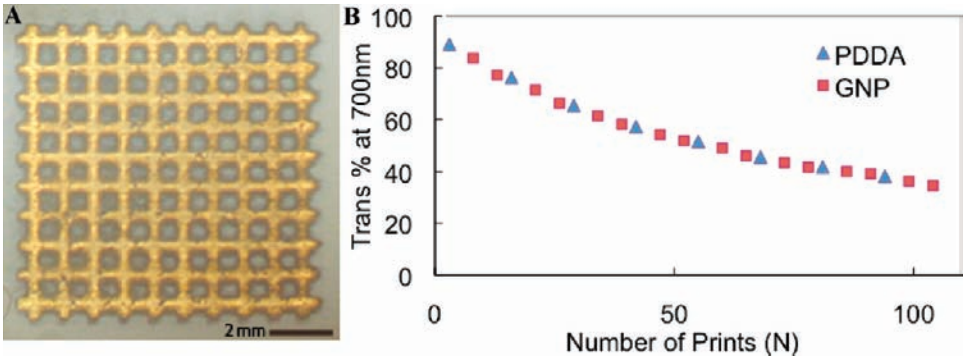

Figure 6. (A) Photograph of $(PDDA^{3}/GNP^{10})_4$ multilayered nanocomposite formed using LBL technology and patterned with inkjet printing. (B) Dependence of UV−vis transmission of the grid pattern on the total number of printed layers, *N*. Measurements were taken after every 3 prints of PDDA and 5 prints of GNP.

This indicates a much-improved degree of control over the multilayer structure with inkjet LBL over the dip modality.

Patterned Nanocomposites. In addition to controlling the NP coverage of each layer, the controlled droplet delivery of inkjet printing provides the opportunity for additive patterning with simple introduction of multiple computer-generated patterns and components that are attractive for advanced material manufacturing. As a demonstration of this capability, we deposited GNP features of various sizes by printing four lines of decreasing computer-generated widths of 425, 283, 168, and 66 μm with 3 prints of 0.0025 wt % PDDA and 75 prints of the GNP dispersion, i.e. $(PDDA^{3}/GNP^{75})_1$, onto a silicon substrate (Figure 5). The goal of this test was to establish the limits of patterning well-resolved lines with a simple desktop printer and the LBL technique. As expected, the smaller the computer-generated feature becomes, the less precise the actual deposited line. Interestingly the reduction of the line width is accompanied by a lower average density of GNPs, which is attributed to specific droplet size control programs employed by Epson (Figure 5). Although this patterning effect is printer-specific and much higher resolution and droplet control can be obtained with advanced inkjet systems, it is still quite important to realize that some structural parameters of the coatings can become coupled in the inkjet modality of LBL while being fairly independent in the dip-coating LBL technique. Interesting to point out based on Figures 4 and 5, there is apparently no strict and specific ratio of polymer to NPs that results in stable layers; we believe that a wide range of ratios could be used. At the same time, if only one component is deposited multiple times, the pattern is washed immediately off during the single finishing rinse step.

In order to demonstrate the ability of the inkjet technique to simultaneously produce and control the spatial arrangement of multilayered nanocomposites, a grid pattern designed with a 0.3 mm line width was printed from 0.0025 wt % PDDA and GNP LBL (Figure 6A). Each bilayer was composed of $x = 3$ prints of PDDA followed by $y = 10$ prints of GNPs. Light transmission at 700 nm was observed three times during each bilayer to observe the growth of the film: after the deposition of 3 prints of PDDA and after 5 and 10 prints of gold. UV−vis transmission data were then plotted against the number of prints (*N*) to demonstrate the continued growth of the film (Figure 6B). The nanocomposite LBL grid was then washed and dried, leaving behind a multilayer composite with not only controlled GNP composition in each layer but also controlled 3D spatial arrangement. Although, the transmission of the pattern rose from 34.6 ± 0.4% to 43.4 ± 0.5% after washing, this test clearly demonstrates the ability of inkjet LBL to create insoluble, multilayered nanocomposite patterns.

Comparison with Other Methods of Patterning of LBL Films. A number of approaches to spatially control LBL-assembled multilayers to create lateral patterning have been explored.[6] For example, patterned surface chemistries created by microcontact printing,[52−54] dip-pen nanolithography,[55] nanografting,[56] and electron-beam lithography[57] were used to guide the spatially selective growth of LBL assembled multilayers. Electric field directed LBL assembly[58] and spin-assisted LBL combined with with microfluidics[59] were also used for selective deposition of LBL multilayers. Alternatively, spatially selective removal of LBL multilayers was used for patterning based on the selective dissolution of pH sensitive films with inkjet printing,[23] assembly atop patterned substrates with selective

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removability created by nanoimprinting[60] or photolithography,[61] selective photo-cross-linking,[62,63] and traditional lithographic patterning.[64] Finally, stamps used in either compression[65,66] or multilayer transfer printing[67] have also successfully created multilayer patterns.

Inkjet LBL corresponds to simultaneous multilayer growth and patterning. In respect to the characteristic size of the features, traditional lithography and nanoimprinting have better *X*-*Y*. However, unlike them and most LBL patterning modalities mentioned above, it is a continuous additive technique with corresponding advantages and disadvantages. It is also exceptionally simple and can be realized using minimal hardware investments with immediate results. It has the capability to serve as a universal patterning technique for LBL as it does not rely on specific chemical functionalities or templates such as stamps or masks that limit the material choice, number of components, levels, and designs currently possible. The additive approach of inkjet LBL printing can in many cases reduce the number of processing steps while increasing process flexibility where patterns are generated from electronic data rather than premade templates.

One of the disadvantages of inkjet LBL is that it is primarily applicable when the total area of LBL coating is relatively small. The task of coating large and highly curved areas with continuous LBL multilayers is probably better served by one of the traditional techniques.

One also needs to point out that regardless of the absence of the "coffee ring" effects in our case of $(\mathrm{PDDA}^x/\mathrm{GNP}^y)_z$ (Figure 4), the possibility of its occurrence needs to be considered and will require fine-tuning of the ink and the droplet parameters. In addition, multicartridge and -nozzle systems that allow for incorporation of a large variety of components in LBL layers can be fairly complex and expensive although feasible.

Conclusions

As a result of this study, it has been demonstrated that inkjet technology can be successfully used to modify LBL assembly by eliminating most intermediate rinsing steps with accurate dispensing of the LBL components to the required area of the surface. In addition to providing some insight into the basics of LBL, the data collected indicate the ability of this approach to vary the surface coverage of GNPs and retain the overall linearity of GNP deposition characteristic of traditional LBL methods. The comparison of $(\mathrm{PDDA}^x/\mathrm{GNP}^y)_z$ and $(\mathrm{PDDA}/\mathrm{GNP})_z$ multilayers also shows that (at least in some cases) the localized dispensation of the required amounts of LBL components will lead to marked improvements of the surface density of NPs. It can also lead to wider ranges of particle−polymer ratios.

The patterning and stability of the inkjet LBL films also indicate that this method can provide a promising alternative for multilevel patterning with nanoscale control of stratification. In traditional inkjet printing of electronic devices there is a long-standing problem of production of multicomponent, layered structures. The common solvents of many inks with electro- or photoactive components result in redissolution and mixing with predeposited layers. Low temperature phase-changing inks, polymer binders, UV curing or reacting inks, thermal treatments, and orthogonal solvents[68−70] were used to prevent redistribution of the solute between layers, but these inks correspond to a relatively small set of systems and oftentimes significantly change the properties of the deposited layer. Even under special conditions the thickness of individual strata that can be deposited is seldom smaller than 100 μm.[68,71−73] Inkjet LBL allows stratified multilayers to be assembled into stratified multilevel structures with the accuracy determined by the thickness of the individual bilayer (Figure 3) and diameter of NPs (if any) without any problems associated with redissolution or complex chemistry associated with the use of orthogonal solvents or special inks. This will be an essential advantage for the future development of inkjet LBL due to the significance of multilevel nanoscale coatings on flat substrates in the production of flexible electronics and energy conversion devices. Further optimization of the inkjet LBL technique toward advanced material production and a better understanding of the methods of structural control in such multilayers are also anticipated.

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