

Automated spin-assisted layer-by-layer assembly of nanocomposites

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We present the design and verification of a desktop system for the automated production of nanostructured thin films via spin-assisted layer-by-layer (spin-LBL) assembly. The utility of this system is demonstrated by fabricating polyvinyl alcohol/clay nanocomposites. Ellipsometry measurements demonstrate that the automated spin-LBL method creates composites with bilayer thickness and growth rate comparable to traditional dip-LBL; however, the cycle time of the spin-LBL method is an order of magnitude faster. Small angle X-ray scattering analysis shows that the clay platelets in spin-LBL nanocomposites are more highly aligned than in dip-LBL composites. This method can significantly increase the throughput of laboratory-scale LBL discovery and processing, can enable testing of functional properties of LBL nanocomposites over wafer-scale areas, and can be scaled to larger substrates for commercial production. © 2009 American Institute of Physics. [DOI: 10.1063/1.3078009]

I. INTRODUCTION

Layer-by-layer (LBL) assembly is a well-established technique for production of multilayered thin films.¹ In LBL assembly, oppositely charged compounds are sequentially built on a surface [Fig. 1(a)] in layers having nanometer-order thickness. LBL has been used to create nanostructured materials for myriad applications including structural composites, filtration membranes, functional coatings, tissue scaffolds, solar cells, and batteries.²

LBL assembly is traditionally performed by repeatedly dipping a substrate in a series of solutions [Fig. 1(b)]; for example, the dip cycle alternates between solutions of positively charged and negatively charged molecules, separated by a water rinse and/or a drying step. While versatile, this method can be very time consuming because the cycle time is limited by the rate of fluid adsorption on the substrate, so a single layer can take up to several minutes to apply. Hundreds of layers are needed to produce even micron-thick films, and therefore the total film growth process can take days.

LBL assembly has also been performed using other deposition strategies. In spin-assisted LBL assembly, a substrate is rotated rapidly while the LBL sequence is injected onto the substrate [Fig. 1(c)], typically using a nozzle impinging upon the center of the substrate.^{3,4} The rapid spinning of the sample produces thin layers over the full substrate area. Because of the centrifugal force acting on the liquid layer, molecules adsorb on the substrate on the order of seconds, which is much faster than in the dip-LBL process.³ Additionally, it has been found that the films

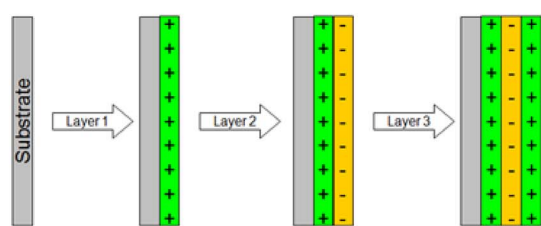
produced with spin-LBL assembly have a more highly ordered internal structure than dip-coated materials.³ Thus, spin-LBL can reduce production times by orders of magnitude and increase film quality, thereby readily enabling exploration of thicker nanocomposites. In another alternative to dip-LBL assembly, Krogman *et al.* developed an automated machine for LBL deposition using a spray technique that is 25 times faster than the dip-coating method.⁵

Here, we present a desktop apparatus for automated spin-LBL assembly, which accommodates substrates with diameters up to 10 cm. This system can be preprogrammed for an indefinite number of layers, with control of the deposition sequence, the dispensed volume, and the substrate spin rate of each step. We use this “Spin-Grower” system to fabricate polymer-clay nanocomposites, and demonstrate that these materials have higher structural order than nanocomposites fabricated by the traditional dip-LBL method.

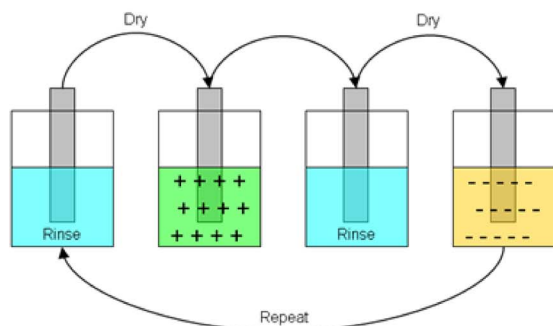
II. SYSTEM DESIGN AND CONSTRUCTION

The Spin-Grower system was custom-built using a commercially available spin coater (Specialty Coating Systems G3P-8) and peristaltic pumps (Watson Marlow 314D), and is controlled using LABVIEW software (National Instruments) with hardware interface boards (NI USB-6008 DAQ). Figure 2 shows a functional diagram of the system, Table I lists the system specifications, and Fig. 3 shows the system in our laboratory. The system has five independent flow channels and solutions can be introduced in any user-specified sequence. The LABVIEW program controlling the pumps allows the user to specify injection rates and times for each solution as well as the drying time between each injection step. The pumps are organized in a custom-rack made of aluminum sheet, and all electronics are stored in a centralized electron-

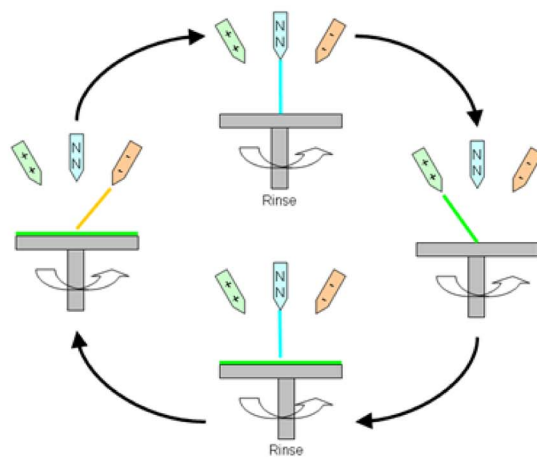
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(a)



(b)



(c)

FIG. 1. (Color online) LBL assembly is accomplished by sequential layering of cationic (+) and anionic (-) solutions onto a substrate as shown in (a). Traditional methods of LBL assembly use a dipping technique to deposit the films, shown schematically in (b). Spin-assisted LBL, wherein alternating compounds are injected onto a rotating substrate, is illustrated in (c).

ics box. Five 4 l bottles (Nalgene) containing chemical solutions are rested on top of the pump rack, and Bioprene tubing (Watson Marlow) is used for fluid routing.

The pumps use rollers to create a positive displacement in the fluid tubing.⁶ Peristaltic pumps were selected for this application because their moving parts do not contact the fluid because of their capacity for precise and highly repeatable flow control, and because the pumps can be easily reversed to prevent unwanted dripping from the nozzle after the injection event. The speed of each pump is directly controlled by a voltage signal from the LABVIEW software. At the end of each fluid deposition cycle, the motor is reversed

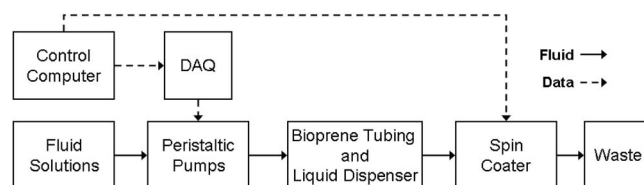


FIG. 2. Functional diagram of Spin-Grower system, showing the flows of fluid and data.

momentarily so that no extraneous fluid drips onto the substrate.

A new cover for the spin coater was fabricated to accommodate placement of the five fluid lines over the substrate. Each Bioprene tube passes through a Loc-Line (Lockwood Products) tube which is attached to the cover. The Loc-Line can be manually articulated to the desired injection position and incident angle over the substrate. Finally, a vacuum chuck adapter made of Delrin facilitates optional use of glass slide substrates, which are typically used in dip-LBL.

III. CALIBRATION AND OPERATION

A. Flow calibration

The flow control for our system is open loop so the pumps were calibrated before LBL operation. Assuming all fluids of interest for LBL deposition will have viscosities similar to that of water, the flow rates were calibrated using distilled water. To perform the calibration for each pump, fluid was injected into a beaker while the pump was operated at the nominal voltages suggested for flow rates of 15, 30, 45, 60, and 75 ml/min. The expected mass of the fluid in the beaker was then compared to the actual mass dispensed. A linear fit was then used to determine the appropriate voltage-flow relationship. Figure 4(a) shows the expected versus experimental volumes before and after calibration.

To ensure that no extraneous fluid drips onto the substrate after the injection is complete, the motor is reversed to draw the fluid away from the open end of the tubing. Due to the motor inertia, the minimum reversal motion varies with the injection rate, and this must also be calibrated. This calibration is performed by finding the minimum pump reversal time needed to suck the solution pendant drop such that the fluid meniscus tip is flush with the end of the tube. Figure 4(c) shows that the LABVIEW input voltage empirically follows a quadratic relation to reverse time correction factor. Alternatively, using pumps with active braking may shorten the pump reverse time or eliminate the need for this calibration.

TABLE I. Summary of Spin-Grower technical specifications.

Specification	Value	
Substrate spin speed	1000–10 000	RPM
Maximum fluid injection rate	1.2	ml/s
Maximum substrate diameter	10	cm
Number of solutions	5	qty
Reservoir capacity (each)	4	L
Solution pH range	1–10	pH

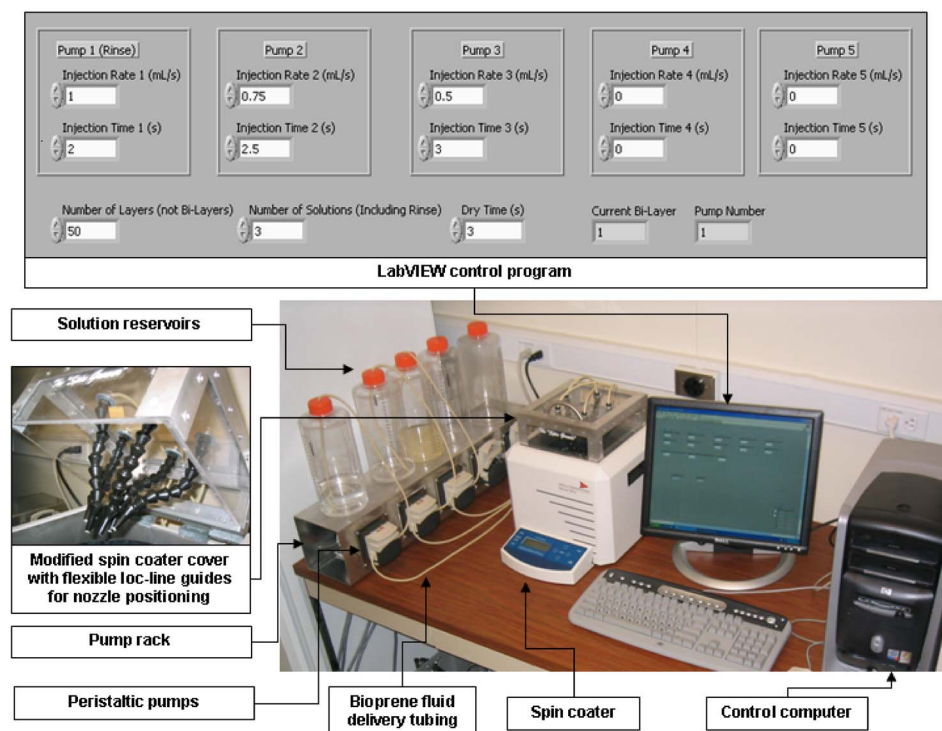


FIG. 3. (Color online) Spin-Grower system, showing major components and close-up images of modified spin coater cover and control program.

B. Film production

To set up the Spin-Grower for film production, the user must first fill the solution bottles with the desired solutions, and purge the fluid lines leading into the spin coater. The substrate is then loaded onto the spin coater chuck, either directly or using the chuck adaptor, and held in place with the vacuum system incorporated into the spin coater. The desired parameters for number of layers, fluid flow rates and flow times as well as dry times (spinning without fluid flow) are specified in the LABVIEW control panel, and the spin speed is specified in the spin coater software. Once the spin coater reaches the desired speed, the fluid deposition program can be executed. The Spin-Grower requires no further attention until the process is complete.

IV. FABRICATION OF POLYVINYL ALCOHOL/CLAY NANOCOMPOSITES

To demonstrate the utility of the Spin-Grower system for LBL assembly of nanocomposites, films of polyvinyl alcohol (PVA) and clay were produced both using the traditional dip-LBL method, and using the Spin-Grower.

A. Materials and methods

PVA (molecular weight (MW) $\approx 70\,000$) was purchased from Sigma-Aldrich (St. Louis, MO). Na⁺-Montmorillonite (MTM) powder was purchased from Southern Clay Products (Gonzales, TX). Microscope glass slides (7.62×2.54 cm²) were obtained from Fisher Scientific. Hydrogen peroxide, concentrated sulfuric acid and concentrated hydrofluoric acids (HF) were purchased from Sigma-Aldrich. A dispersion of 0.5 wt % MTM was prepared by dissolving 5 g of clay in 1 l of de-ionized water (DI water), under vigorous stirring for 1

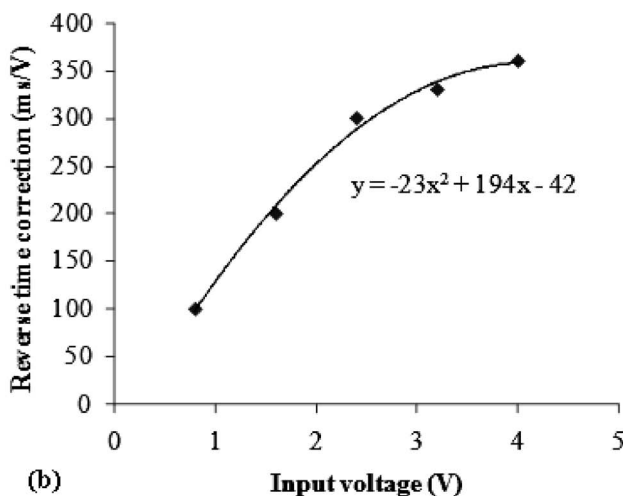
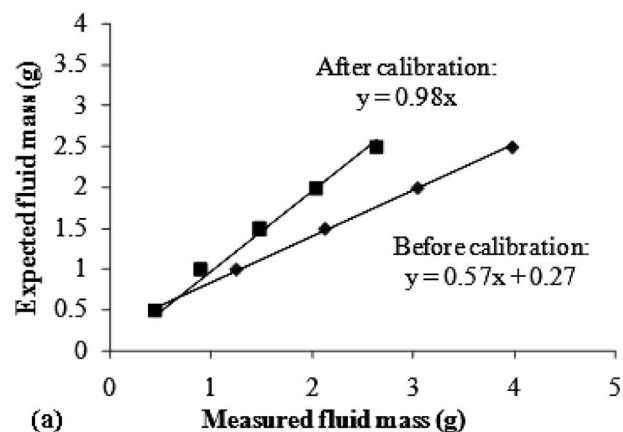


FIG. 4. (a) Pump fluid deposition mass characterization curves before and after calibration. (b) Reverse time correction factor shows a quadratic relationship with input voltage.

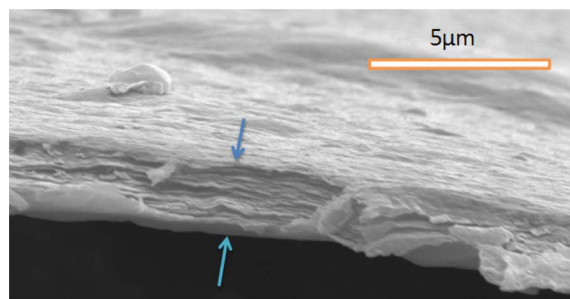


FIG. 5. (Color online) Cross-sectional SEM view of a 300 bilayer, free-standing PVA/clay film made using the Spin-Grower.

week prior to use. After 1 week, the supernatant was collected after the insoluble fraction was allowed to sediment.

Before the deposition of PVA/clay films, the glass slides and silicon wafers for LBL were soaked in “piranha” solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$, 3:1 volume ratio) overnight. Normal dip-LBL films were prepared using a robotic dipping machine, (nanoStrata StratoSequence IV). A clean slide was dipped in PVA solution (1 wt %) for 5 min, rinsed twice with DI water for 1 min each round, and dried with compressed air for 1 min; then dipped in clay solution (0.5 wt %) for 5 min, rinsed twice with DI water for 1 min each round, and then dried for 1 min. This cycle was repeated until 300 bilayers were deposited.

PVA and clay solutions with the same concentrations were used for spin-LBL deposition. A spin speed of 2000 rpm was used throughout the process. First, PVA solution was deposited onto the substrate surface for 4 s at a rate of 0.17 ml/s and then the glass slide was dried (by spinning without fluid injection) for 20 s; then the substrate was rinsed with DI water for 4 s at a rate of 0.2 ml/s and then dried for 20 s. The same sequence was then used for clay using an injection rate of 0.23 ml/s. The cycle was repeated until 300 bilayers were deposited. Freestanding films were detached from the glass slides using 1% HF solution, as described in further detail in Ref. 7.

For the first several bilayers, the film thickness was measured by ellipsometry (BASE-160 Spectroscopic Ellipsometer, J.A. Woollan). The samples for ellipsometry were prepared on silicon wafers, using the same LBL sequence detailed above. Scanning electron microscopy (SEM) images were taken using a FEI Nova Nanolab dual-beam system. Small-angle X-ray scattering (SAXS) studies were performed at the G1 beamline station at the Cornell High Energy Synchrotron Source (CHESS). The wavelength of the x rays was 0.1239 nm, and the sample to detector distance was calibrated with silver behenate (first order scattering vector of q of 1.076 nm^{-1} , with $q=4\pi \sin(\theta/\lambda)$ where 2θ is the scattering angle and λ is the wavelength). A slow-scan charge coupled device-based x-ray detector, home built by Tate and Gruner of the Cornell University, Physics Department, was used for data collection.

B. Film characterization

SEM imaging (Fig. 5) shows the stratified structure of the spin-LBL films, wherein clay platelets form packed layers parallel to the adsorption surface. The average thickness

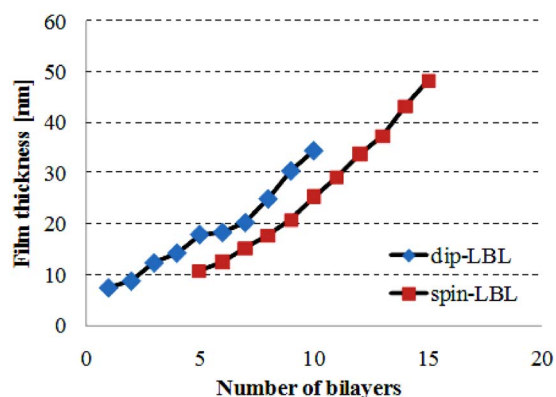


FIG. 6. (Color online) Initial growth kinetics of PVA/clay multilayers produced by automated spin-assisted LBL and dip-assisted LBL. The data for the dip-LBL film is from Podsiadlo *et al.* (Ref. 8).

of the film with 300 bilayers was approximately $1.5 \mu\text{m}$, which is similar to that of the dip-LBL film.⁸ However, ellipsometry and SEM measurements showed issues with spatial uniformity of the spin-LBL film thickness, especially for films thicker than $1 \mu\text{m}$. For example, the thickness of a 20 bilayer film measured using ellipsometry ranges from 46.4 to 49.2 nm. The thickness of a 300 bilayer film measured using SEM ranges from 1.0 to $2.0 \mu\text{m}$, with the average thickness of $1.5 \mu\text{m}$. The uniformity of the films is related to the experimental conditions such as spin speed, spin time, and solution concentration. We are still determining the experimental conditions that minimize the film thickness variation.

Successful adsorption of PVA/clay multilayers was also characterized with ellipsometry (Fig. 6). The film thickness increased linearly from 5 to 15 bilayers, which showed a similar trend as that of dip-LBL films of PVA/clay.⁸ It should be noted that while most LBL films show linear growth, some grow nonlinearly. For example, films of poly(ethyleneimine), poly(acrylic acid), and Na^+ -montmorillonite show exponential growth rates.⁹ However, in the PVA/clay case, both the spin- and dip-LBL assembly methods show similar linear growth.

SAXS was used to investigate the internal layering structure of the multilayer films (Fig. 7). For PVA/clay film by dip-LBL and spin-LBL, the primary scattering peaks were observed at 2.79 and 2.76 nm, respectively, along with several higher order reflections. This result indicates that the spin-LBL method reduces the intercalation of polymer between clay sheets. Additionally, we can quantify the orientation of the clay platelets using Herman’s orientation parameter (f).^{10–12} To calculate the orientation parameter, azimuthal scans were taken over a small window around the q range of interest. This parameter ranges from 1 to $-\frac{1}{2}$, in which a value of zero indicates a completely random distribution of orientations. When f is 1 or $-\frac{1}{2}$ the system is completely aligned parallel or perpendicular, respectively, to the chosen reference direction, which in this case is perpendicular to the substrate. As listed in Table II, the spin-LBL PVA/clay film showed a higher Hermans orientation parameter (0.83 ± 0.03) than the dip-LBL film (0.62 ± 0.05). Thus, the clay platelets in the spin-LBL film display higher orientation than that in the dip-LBL sample. In dip-LBL the components

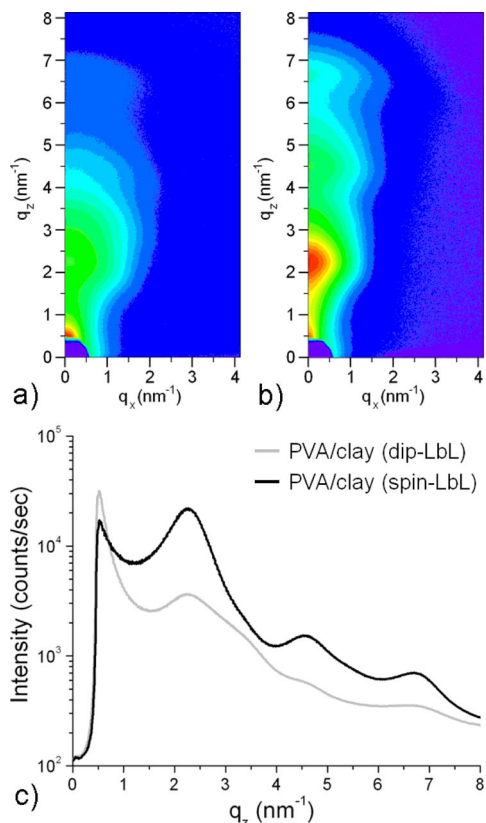


FIG. 7. (Color online) Two-dimensional SAXS patterns of 300 bilayer free-standing PVA/clay films: (a) composite made by dip-LBL; (b) composite made by spin-LBL. (c) one-dimensional scans of the SAXS patterns shown in (a) and (b) along the q_z direction.

are simply adsorbed onto the surface, and the minimization of surface energy results in the orientation of the clay platelets parallel to the substrate. For spin-LBL the high fluid velocity over the substrate creates shear forces during the film deposition, resulting in the increased orientation of the clay platelets.

V. CONCLUSIONS

We have created a desktop-scale machine (Fig. 3) for the rapid automatic LBL assembly of nanostructured composites via spin-coating. The machine has successfully produced PVA/clay nanocomposite films (Fig. 5). Ellipsometry measurements of film thickness verified that the spin-coating method achieves LBL assembly. Additionally, comparison of spin-LBL films with traditional dip-coated LBL films using

TABLE II. Summary of SAXS data for the PVA/clay nanocomposites, showing higher structural order in the spin-LBL films.

	PVA/clay (dip-LBL)	PVA/clay (spin-LBL)
q (nm^{-1})	2.254	2.278
d spacing (nm)	2.79	2.76
Herman's orientation parameter (f)	0.62 ± 0.05	0.83 ± 0.03

SAXS indicates that clay platelets in spin-LBL are more highly ordered than in the dip-coated LBL films (Fig. 7), suggesting that the spin-LBL films may have higher mechanical properties.

The automated spin-coating technique also decreases LBL assembly time by an order of magnitude compared to the traditional dip-LBL method. This could greatly accelerate the pace at which new nanostructured thin films for a variety of applications can be developed and studied. This method could also be easily scaled to larger substrates, rapidly creating films over a large surface area, which is important for commercial viability. The rapid production rates combined with the high-quality films produced using the spin-LBL method create the potential for new, thicker multilayer nanocomposites having novel morphologies and properties.

ACKNOWLEDGMENTS

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