**High-Throughput and Versatile Design for Multi-Layer Coating Deposition using Lab Automation Through Arduino-Controlled Devices**

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**Abstract**

Laboratory and experimental scale manufacturing processes are limited by human error (e.g., poor control over motion, personal subjectivity); especially under fatiguing conditions involving precise, repetitive operations, incurring compounding error. Commercial layer-by-layer (LbL) automation devices are prohibitively high-priced (esp. for academic institutions) with limited flexibility in form factor and potentially software-associated constraints/limitations. In this work, a novel automated multi-beaker dip coater was fabricated to facilitate the nano cerium oxide/polymer coatings via an LbL dip coating process and the synthesis of nano ceria films via a novel successive ionic layer adsorption and reaction (SILAR) method on glass substrate. Automation of tasks, such as those mediating the detailed procedures, is essential in producing highly reproducible, consistent products/materials; as well as to reduce the time commitments for laboratory researchers. Herein we detail the construction of a relatively large, yet inexpensive, LbL coating instrument which can operate over 90 cm in the horizontal axis: allowing, for example, up to eight 200 mL beakers with accompanying stir plates. The instrument is operated by simple “off-the-shelf” electronics to control the path and timing of the samples with open-source software, while providing precision at ± 0.01mm. Further, 3D-printed components were used to maximize the number of substrates that could be coated simultaneously: further improving sample production rate and reducing waste. Further possibilities for automation beyond the detailed device are provided and discussed including software interfaces, physical control methods, and sensors for data collection/analysis or for triggers of automated tasks.

**1. Introduction**

Layer-by-Layer (LbL) assembly can produce nanoscale thin films, or even sub-nanometer thickness in certain conditions, on a desired substrate by dipping the substrate into two or more liquids or solutions repetitively. In 1997 it was shown that the LbL assembly process could be used to modify the surface of poly(ethylene terephthalate) (PET) with polyelectrolytes at a precision of 2-6Å1. The investigation of self-assembled thin films is of particular interest due to the unique properties displayed by these films compared to their thicker counterparts (e.g. enhanced chemical reactivity, optical character, bandgap/semiconducting character, etc.)2. However, 3D nanoscale control of structures remains a difficult task. Alternatively, repetitive application of 2D nanoscale thin film structures may be achieved by using LbL assembly, enabling nanoscale precision of the final 3D layered nanostructure3. These nanoscale structures are assembled by depositing oppositely charged particles, polymers, proteins, etc., in alternating sequence. The method of LbL assembly (e.g. immersive, spin, spray) has been shown to alter the characteristics and performance of the final coating4. The key factor in any LbL assembly method is the uniformity of the layers which then increases the predictability of the performance during an application. These LbL assembled films have a variety of applications in the medical field as time released drugs/therapeutic agents in pills and on medical implants5, antimicrobial films on temporarily inserted devices such as catheters or as intravenous fluid delivery systems, stem cell research6, among other essential medical technologies/methods7. Other applications may include catalysts for chemical reactions8, decomposable oxygen barriers for ecofriendly food wrap9, fire retardants10, modification of optical properties, etc.10

If the LbL process is done manually, the solutions must be rotated in and out of the breaker path of a single axis dipping device by a human. The requirement of repeated manual operations compounds related sources of experimental error, increasing with film thickness (increasing numbers of layer pairs). Further, the researcher must be physically present to rotate out each beaker requiring substantial time dedication to the process by an operator. Any variation in dipping speed decreases the uniformity of the sample, affects the collected data and any correlations that might be found. For thicker coatings, the sequence of solution dipping, including washing steps, must be repeated potentially requiring 100 hours or more. The manual labor time involved in the process is prohibitive, as is the expense of process automation for the majority of research laboratory budgets. Nanoscience and technology research is resource-intensive and particularly sensitive to error and variation in the manufacturing process, suggesting a need for improved data quality, in conflict with resource limitations.

At the industrial manufacturing scale, human error and labor have been largely removed through process-wide automation11. Laboratories can save money two-fold by creating their own automated LbL dip-coating device, once on the upfront cost, and again in ongoing labor costs as the device continues to be used. The automation will thereby reduce requirements of operator attention: allowing focus to be redirected to more complex, dynamic tasks or those requiring dexterity. The need for automation of the dip coating processes is apparent by the many commercial devices already on the market for this purpose, and their high price. Basic single-beaker programmable dip coaters sell for several thousands of dollars (USD) (https://www.mtixtl.com/DesktopDip CoaterwithvariableSpeed1-200mm/min-PTL-MM01.aspx, accessed 31 May 2021) and most multi-beaker systems typically sell for tens of thousands of dollars (https://www.mtixtl.com/PTL-SC-6S-LD.aspx, accessed 31 May 2021). A further drawback of all these systems is that operation is confined to the programmable specifications or physical limitations of these commercial devices.

A potential solution, bypassing monetary and industrial constraints, is the development of analogous instruments from inexpensive commercial components, designed to the user’s unique criteria. The device must be simple, to be quickly and easily used by researchers across disparate fields, while enabling the execution of varied, complex dipping sequences/operations. This device’s value will surpass that of commercial devices due to its fully customizability of dipping sequences, large beaker capacity, customizable multi-sample holder, ability to add extra sensors and upgrades and its simplicity, enabling the ability to be fixed by the lab technician rather than waiting for repair by a third party. In the detailed processes, this was accomplished using “off-the-shelf” microcontrollers with prebuilt libraries of human readable/interpretable code. By using these components, movement of the device can be controlled with a line of code as simple as “boardA.moveTo (Position2)”.

Microcontrollers, smaller and simpler versions of regular computers, can control external motors, collect data from sensors and communicate data to other devices or to consumer scale computers. The Arduino microcontroller is open source (https://www.arduino.cc/en/guide/

introduction, accessed 31 May 2021) and its coding language is easy to use. In large part this is due to the high number of Arduino compatible devices, such as motor control boards that come with libraries of code prewritten by the manufacturers of the compatible devices. This allows for streamlined operations of the peripheral devices such as the Sparkfun Autodriver L6470 (www.sparkfun.com/products/13752, accessed 31 May 2021) which controls a stepper motor by modulating power to the motor’s coil windings (www.monolithicpower.com/en/stepper-motors-basics-types-uses, accessed 31 May 2021).

Advances in the last decade have enabled higher quality 3D prints at steadily decreasing costs. Advances in model slicing software (https://www.simplify3d.com/support/articles/3d-printing-gcode-tutorial/, accessed 31 May 2021; (https://help.prusa3d.com/en/article/general- info\_1910#\_ga=2.255943883.1327618739.1616192379-1806373664.1616192379) accessed 31 May 2021) vastly improve 3D print quality and have reduced setup time and troubleshooting needed to less than 15 minutes. 3D printing allowed for the inexpensive design, fabrication and testing of substrate holding components of the device with the optionality of slots for sensors, positioning lasers, as well as structural fasteners.

The developed coating devices essential to investigate the using different polymers, nanoparticles coated on substrate at various environmental conditions. For that, we have chosen cerium oxide nanoparticles along with polymers such as chitosan and poly (acrylic acid) for layer-by-layer coating process. Ceria nanostructures have been used for various applications due to their unique regenerative oxidative properties via inter-conversion of cerium atoms between 3+ and 4+ oxidation states. In an earlier study, we have reported antioxidant characteristics of ceria thin films coated by atomic layer deposition (ALD)12. Until now, the techniques used for thin-film LbL ceria deposition usually requires sophisticated equipment, inert atmosphere, high vacuum, and expensive precursors13, physical vapor deposition (PVD)14 and chemical vapor deposition (CVD) 15, but they all share the same limitations as ALD (e.g. requiring sophisticated instrumentation, inert atmosphere, high vacuum and expensive precursors). Successive Ionic Layer Adsorption and reaction (SILAR) coating methods are not limited by these issues and can allow controlled ceria thin film layer deposition, as reported previously for ceria films by Khan et al.16. Although the work has opened a new direction for ceria thin film coating, the required post-process heating at high temperatures in a furnace to effect phase formation/crystallization between layer depositions can limit thin film quality and practicality. Herein we report a fully automated SILAR ceria process that doesn’t require any post-process heating for phase formation/ crystallization.

This work will detail the assembly of this LbL dipping device’s mechanical, electrical, and software components. The reliability of the device is shown over a 34 hour, 20 bi-layer LbL coating of a polymer infused with nanoparticles. In a second use case, a SILAR16 method was used to create layers of ceria NPs using NaOH and cerium nitrate in a two-step process at room temperature.

**2. Materials**

**2.1** Arduino Controlled Devices Fabrication

***Physical parts***

The linear actuator bundles (Parts 1A and 1B, Table 1), make up most of the mechanical parts of the device. These packages included the Nema 23 stepper motor and Acme lead screw, as well as the rail track and parts for the gantry plate connection that facilitates bi-axial motion. The Arduino Mega2560(Part 2A), SparkFun L6470 Autodrivers (Part 2B) control the device and regulate the power to the motors respectively. The motors and auto drivers are powered with one 120 AC to 12v DC power converter (Part 2C). Limit switches, laser, and flight of time: distance sensor, were used to reduce the time required for setting up an experiment.

***Software***

The Auto driver L6470 code library was used for motor control as provided by sparkfun.com. The arduino IDE software is an environment for building arduino code and Visual Studio Code was used for building the python-based GUI. Python Libraries, Tkinter and pillow, for the GUI and image management, respectively, aided in rapid development.

***3D Printing***

3D models created in AutoCAD 2020 student-version (Part 6C) were turned into physical parts with the MK3 Prusa 3D printer by Josef Prusa, using Prusa made PLA filament (Part 5A, 5B respectively). Prusaslicer (Part 6D) was used to transform the model into 3D printer instructions.

**2.2 Materials for layer-by-layer (LbL) and SILAR coating**

Poly (acrylic acid) (PAA), low viscosity chitosan (Chi), cerium nitrate hexahydrate (99.99% pure), sodium hydroxide (99.99% purity), sodium chloride and sulfuric acid were obtained from Sigma-Aldrich. The glass slide was purchased from Fisher Scientific and Esco optics. Deionized water (resistivity >18 megaohm) was used. All chemicals were used as received.

**3. Methods**

**3.1 Assembly overview**

The computer-based interface (Fig. 1a), built in python3 code using the tkinter library, controls the Arduino (Table 1: Part 2A), which relays commands to the L6470 autodriver control boards (Table 1: Part 2B) that pulse electrical signals to rotate the motors.

**3.2 Assembly of Actuators**

The assembly of the linear actuator bundles follows the guide provided by Openbuilds.com (https://openbuilds.com/builds/c-beam%C2%AE-xlarge-linear-actuator.7424/, accessed date May 31, 2021). The gantry assemblies move as their respective nut blocks are driven by lead screws17. The gantry assemblies were removed from their axes and attached together with m5 screws and then reconnected with their respective axes. The X-axis supports the Z axis which is free to move left and right as the motor for the former rotates. The X-axis is supported by V-beam rails connected at the ends where 8mm m5 screws, corner brackets, and tee nuts were used to attach the device to the supports.

**3.3 Wiring Components**

**Motors - Power- L6470**

Wires from the motors (Fig. 1b: 1A,1B) were connected to the L6470 Autodrivers (Fig. 1b: 2B), which were wired in series to the Arduino Mega 2560 (Fig. 1b: 2A) using SPI connections (https://www.arduino.cc/en/reference/SPI, accessed date May 31, 2021). The Sparkfun Autodriver website has a detailed guide to help with these connections (https://learn.sparkfun.com/, https://learn.sparkfun.com/tutorials/getting-started-with-the-autodriver). Screw terminals were soldered to the short ends of the Autodrivers where there are spaces for connecting 12v-48V DC power. The AC to DC power supply unit (Fig. 1b: 2C) was connected to the power input terminals, labeled “Motor Power” on the Sparkfun Autodriver red board.

**3.3.1 Limit Switch**

The limit switches (Fig. 1b: 1C) are simple 3 wire devices, one wire to ground, another for the control voltage and lastly, a signal output for when the switch is triggered. These switches are enabled in the Arduino by labeling the pin with an “INPUT” attribute (Appendix 2a). Wires for the switches were run down the device and secured using electrical tape to eliminate wire snags, a potential critical failure point.

**3.3.2 Laser Diode**

The laser diode (Fig. 1b: 3A) has 2 wires, one ground and the other Voltage Common Collector/input signal. When VCC pin voltage is set to “HIGH” the arduino powers on the 25mA laser (Appendix 2b).

**3.3.3 Gas Valve**

The gas valve is a solenoid design18, normally closed, and activates just as the laser diode except that it needs more power than the Arduino Mega 2560 can provide. Extra power is supplied from the AC to DC power supply unit. The operation of the solenoid valve is straightforward except for the backwards electromotive force (EMF) generated when the power to the solenoid is turned off19. To stop this, a small IN4002(https://www.allaboutcircuits.com/textbook/semiconductors/chpt-3/diode-ratings/, accessed date May 31, 2021) diode is placed in parallel from the solenoid valve’s ground wire to the wire acting as the switch. The surge of current generated from the back EMF will flow into the now low voltage, previously high voltage, wire of the solenoid because of the short created by the diode. This loop dissipates the back current due to the resistance of the wires (https://progeny.co.uk/back-emf-suppression/, accessed date May 31, 2021).

**3.4 Interfacing**

Python communicates to the Arduino over a USB serial port, also referred to as a communications port (COM port). Functions were created in which user specified parameters are sent from the python interface to the Arduino using a function with a standardized format(Appendix 3a). The self.sendMe variable begins with a 3 digit code used to identify the proper function to call from the Arduino device. A one size fits all Arduino function, “pullData”(Appendix 2c), is used to capture the incoming data over the serial port and resembles the structure of the python string variable “self.sendMe”. The data transfer between the two programs needs to be synchronized so that once data is sent from one device, the other is already waiting to read the incoming information. When the arduino sends data back to python there is a serial port reading function, “checkBuffer” (Appendix 3b) that captures the data only when the defined starting character is sent, which enables cleaner transfer of information. For simplicity, understand Arduino runs a loop of code, only from a certain section of the program. This loop of code waits for a command from serial connection to the computer (Python3, Tkinter GUI) and only when a command is available to be processed will the Arduino code proceed. This is achieved through a while () loop (https://www.arduino.cc/reference/en/language/structure/control-structure/while/, accessed date May 31, 2021) (Appendix 2d) and the selection of the correct arduino program is done through a “switchcase” (www.arduino.cc/, accessed date May 31, 2021; https://www.arduino.cc/reference/

en/language/structure/control-structure/switchcase/, accessed date May 31, 2021) (Appendix 2e).

**3.5 Creating the Basic Arduino Functions**

**3.5.1 Configuration Function and Speed Settings**

Configuring the motor boards is done with a function in the Arduino code and allows for changing the default values of the Sparkfun Autodrivers. An example can be seen on their website (<https://learn.sparkfun.com/>, https://learn.sparkfun.com/tutorials/getting-started-with-the-autodriver). Several parameters in the configuration function affect the speed of the device include max speed, acceleration, deceleration, and microstepping. All speed settings are in units of steps per second and acceleration/deceleration in steps per second per second. Microstepping is a function of the device which smooths the current pulses to the motor to create a smooth transition between motor steps and is usually used at lower speeds. The condition of the LEAD screw is the limiting factor for the speed of the device at the 1m length(horizontally). If the LEAD screw is bent, it will cause vibration as it spins to move the gantry plate. The longer the LEAD screw, the more it has a natural tendency to sag under its own weight, offsetting the center of mass from the central axis of rotation for the screw. At high levels this vibration can cause the device to lose proper threading between the nut block and LEAD screw. As such, it is advisable to keep the speed of the device under the threshold of this excessive vibration. The current settings for the device in the horizontal and vertical directions are 500 steps/s and 150 steps/s respectively.

The accuracy of the speed of the device depends on the timing method used (quartz crystal, 16MHz). Since the changes in position are kept constant with the mechanical parts of the system, the timing of the pulses to the motor and their accuracy, dictate speed. Quartz crystals have stable physical properties which keep their oscillations constant and are the de facto cost-effective time keeping device used in many military applications and consumer products. The difference in the vibration accuracy compared to the manufacturer's claim of 16MHz is usually within 100 ppm or 0.01%. This figure can change slightly based on temperature and each crystal has minor variations due to imperfect manufacturing.

**3.5.2 Reset Function**

The reset function zeros out the position tracking of the L6470s using the limit switches to ensure the same starting point for each layering experiment. It allows for easily restarting the sequence, no matter where in the process it stopped. Appendix 2f is an example of the reset function using the limit switch, labeled sensor NH (near motor, horizontal), to know when gantry plates reach the starting point. The Arduino then hard stops the device and resets the absolute position.

**3.5.3 Position test**

Everything must be aligned perfectly at the start of the experiment because as the coating program runs there is no feedback for the location of the beakers. Making standard beaker holding templates would allow for quick positioning of the precursor liquids but would only work for a small amount of experimental setups. The position test allows for beakers and positions to be added based on space available and the size of extra equipment needed for certain positions. The position test is easily customizable and uses a laser that allows the user to quickly determine exactly where to locate beakers/stir plates (Appendix 2g). The current configuration of the device with a 1m horizontal actuator allows for 885mm of range and 12 standalone 250mL beakers. In the example located in appendix 2g position 2 is a mathematical equation instead of a set variable due to the 16-bit limitation of the Arduino microcontroller. Overcoming this issue is addressed in section 4.

**3.5.4 Adding Beaker Heights**

The device must understand how much vertical distance needs to be traversed for each unique beaker and position. A VL53L0X distance sensor failed to have the required precision for the task unless the table was coated in aluminum foil. As a replacement, hand measurement must be taken. Variables were created for the maximum height of the bottom of the sample holding base (Hmax), sample holder notch location converted to mm distance (ND, and the heights of each beaker (Hofbeaker). All must be entered by the user and the difference in height must not exceed the maximum traversable distance of the vertical gantry plate. The user must take into account the length of the sample to ensure clearance as the sample moves from one beaker to the next. The traversable distance (td) for any beaker position is td = Hmax-ND-Hofbeaker. To allow for a wider variety of experiments, one simply needs to increase the leg height of the device (increased Hmax) and to increase the length of the vertical actuator. Example of this code, including an error message if distance is too great, is shown in appendix 2h. If experiments are uniform, Hmax and ND become constant, reducing the manual input to Hofbeaker.

**3.5.5 Coating Programs**

The primary goal of this device is to accommodate a wide range of dipping sequences to form thin coatings on substrates. The coating program changes as variables are changed by the device user. If less beakers are used the space between the beakers changes to fully utilize the space below the device and allow for larger beakers or other liquid containers. The timing delays in the coating programs while the motors are actively moving the sample to the target location are crucial for proper communication between the arduino, autodrivers, and stepper motors. The while () function plays a critical role in reducing the time delay by triggering the next step in the code milliseconds after the motor has stopped moving. This shortens the experiment by minutes or possibly hours depending on the amount of steps in the coating process. A function is created for one layer and repeated in the main loop of arduino code. The Z-axis motor is simply commanded to move the sample down, wait for the specified time and back up the same distance to zero out the Z position. The X-axis motor then moves to the next specified position. The memory limitations of the Arduino device prohibit saving the location of each position in the units understood by the Sparkfun Autodriver. Therefore, the position must be calculated at the time of use and then immediately passed onto the autodriver (Appendix 2i). Each position is calculated by taking the total range of the device in microsteps and dividing it by the number of beaker positions plus the whole number remainder, rounding down to the nearest microstep of the stepper motor (https://www.arduino.cc/reference/en/language/structure/arithmetic-operators/remainder/, accessed date May 31, 2021). Once at the end of the layer sequence the X-axis motor should return the gantry assembly to the starting position which can be done by instructing the X-axis motor to return to a position of zero. Manually writing one programmed layer coating experiment is simple (Appendix 2j).

**3.6 Graphical User Interface and control**

The accompanying Graphical User Interface (GUI) software was built using Python due to the language’s availability and compatibility with the Arduino hardware and Arduino coding language. Python is a free, open-source programming language with a robust community of contributors and supporting libraries for many hardware products available on the market. The key features used for this device are the python “tkinter” library for GUI creation and COM port bridging using the “serial” library. Other languages, such as JAVA or C, offer minor improvements in the speed of communication between the Arduino hardware and the software used to control it. These speed improvements are negligible for the dipping device and are far outweighed by the need for proprietary code compilers or lack of compatible versatility in the coding language.

The interface was organized in a way where each of the customizable options were sections grouped together in a top to bottom fashion. The first section includes overarching parameters, max height of the device, number of beakers, number of layers, and the notch number of the sample holder. The next three sections were placed side by side which deal with the time, height, and gas drying variables of each beaker location. When the number of beakers are selected the same amount of beaker positions are reflected in the three sections to aid in reducing user input errors. The fourth section at the bottom of the GUI contains the restset, position test and start buttons.

**3.6.1 Tkinter**

Tkinter (https://docs.python.org/3/library/tkinter.html, accessed date May 31, 2021) is a library for Python capable of creating a GUI interface for executing python scripts. Tkinter comes with predefined methods relating to interface objects such as buttons, drop down menus, check boxes, and pop-up windows. The design of the program will incorporate familiar and standardized graphics within a Microsoft Windows operating environment to reduce the learning curve. The program is laid out in a manner where the required inputs from the user are ordered from top to bottom to create a natural flowing and intuitive user experience (Fig. 2a).

**3.6.2 Organization of the communicated data**

The format of both sides of code (Arduino and Python) must be organized into commands, variable data, and predetermined communication codes that will be sent from python to the Arduino or vise-versa. This was done by creating two data parsers. One parser on the Python side that will combine the chosen variable value with the correct communication code enabling the Arduino to correctly assign the variable. The second parser on the Arduino side uses ASCII symbols to define sections of incoming data. This second parser determines what function to call via the switchcase control structure corresponding with the communication code in the message and can assign the values of the user specified arguments or initiate a program on the dipping device.

The main challenges included working around the limitations of the Arduino microcontroller with regard to the amount of data it can receive and store as well as the timing of reading and clearing the buffer. Each character, number or letter, takes 8 bits, a binary data point of ‘0’ or ‘1’ (https://web.stanford.edu/class/cs101/bits-bytes.html, accessed date: May 31, 2021), equal to one byte, to send to the Arduino via the serial connection (USB) (http://www.asciitable.com/; https://www.azavea.com/; https://www.arduino.cc/en/Tutorial/ BuiltInExamples/ASCIITable, accessed date: May 31, 2021). The filling and clearing of the buffer within the Arduino posed timing issues that initially caused data to be lost during transmission. To elevate this, communication must be deliberate between Python and the Arduino. Enough time must be given between messages for the buffer to fill up and be read by the opposing side of the exchange. After the message characters are processed the buffer needs to be cleared to make way for the next message.

The organization of the Python code starts with the standard declaration of imported libraries and variables at the top of the script. Followed by the Tkinter classes and the visual elements contained within. The declaration of the visual elements such as the buttons and images are organized in the same order, they appear in the GUI from top to bottom (Appendix 3c-g). The declaration of elements and the styling are kept separate within the structure of the code for both ease of use and to alleviate bugs that arose during development. The last section of the Python code, after all of the visual elements related to Tkinter are declared, relates to all of the methods that will be necessary to communicate between the Python program and the Arduino (Fig. 2b).

**3.7 3D Printed Parts**

3D printing provides large-scale manufacturing quality to single unique parts. Using Autocad 2020 Student version, 3D models were designed to attach to the c-beam rail of the vertical linear actuator while being height adjustable on the rail. Various sample-holding 3D prints and long-term sample storage were fabricated. The sample positioning in the holder allows for the electrostatic charges and reactions to take place on one sample’s surface without interfering with the others (Fig. 3a).

The sample substrates used were soda lime/glass slides measuring 76 mm x 26 mm x 1 mm. Five glass slides of this size were determined to be the optimal number to fit in a 250 mL beaker when using electrostatic and/or van der Waals forces for the LbL assembly with limiting factors being the beaker diameter and substrate width. The sample holder’s extended neck features multiple pin slots used to extend the reach of the device for maximizing the coated surface area on each sample (Fig. 3a). The printed pin is a simple, 4.8mm diameter, 25mm long cylinder. At the time of publishing, the design for the sample-holder attachment point (Fig. 3b & 3c) has an easy-mount 5mm pinhole for attaching the sample-holder via its neck and a laser for quick positioning of beakers when the “position test” function is called. These features are easily addable to the device because of 3D printing which also enables rapid prototyping, testing, and design refinement.

**3.8 Experimental Procedure**

**3.8.1 Nano LbL assembly coating on glass slide using Arduino controlled device**

For stock solution preparation, 500 mg of chitosan (Chi) was dissolved in 50 mL of 1% acetic acid containing deionized water. Similarly, 500 mg of poly (acrylic acid) (PAA) was dissolved in 50 mL of deionized water. 2 mg/mL solutions of chitosan, a cationic polymer, and PAA, an anionic polymer were prepared using 0.15 M sodium chloride solution to convert into polyelectrolyte solution. Before coating, the glass substrates were etched with 30% sulfuric acid at 70 ºC for 3 h and then washed with running deionized water. The wet surface of the glass substrate was immersed in the cationic polyelectrolyte/chitosan solution for 15 min, followed by immersion into the anionic polyelectrolyte/PAA solution for 15 min using the above LbL coating system (Fig. 4). After each polymer coating step, the substrate was washed with deionized water three times for 2 minutes. The washing steps removed the unbound cationic and anionic polymers. This process was repeated 20 times to make a 20-layer pair (20 LP) polymer coating on glass substrate. The LbL coated glass substrate was stored at 4 ºC for further analysis.

Furthermore, 2 mg/mL chitosan with 10 mM cerium oxide (homemade water-based cerium oxide nanoparticles (CNPs)) co-solution was prepared in 0.15 M sodium chloride solution and used as a cationic polyelectrolyte during the LbL coating. 2 mg/mL PAA in 0.15 M sodium chloride solutions is used as the anionic polyelectrolyte. These solutions were used in LbL assembly. All other conditions were maintained the same and produced the CNPs embedded Chi/PAA film on glass substrate. Chitosan/ poly (acrylic acid) and CNPs embedded Chitosan/ poly (acrylic acid) films hereafter named as Chi/PAA and CNPs-Chi/PAA, respectively. Chitosan and poly (acrylic acid) are very good positive charged and negatively charged polyelectrolytes20, 21. These polymers have high density of positive and negative charges which helps to create a stronger layer-by-layer coating.

**3.8.2 SILAR Coating Experimental Procedure**

The glass substrate was etched using Piranha solution (3:1 volume ratio of concentrated sulfuric acid and hydrogen peroxide) for 5 hours to clean any residual organic matter on the surface, as well as to activate the surface oxide deposition. For the SILAR process, 90 mL of 5.7 mM cerium nitrate was prepared as ceria precursor, and 90 mL of 0.1 M NaOH solution was prepared as an oxidizer. For the SILAR process, a sequential dipping process was used, as shown in fig. 5. The dipping process was started with ceria precursor solution (for 30 sec) followed by DI water (for 1 min) to wash any extra/loosely interacting ceria precursor. From here, the substrate was then dipped in oxidizer solution and kept at 70 ˚C (for 30 sec), followed by dipping in water (for 1 min) again for washing, completing the four-step deposition cycle22. In situ heating allowed sufficient conversion of hydrated ceria forms to the metal oxide, without further need for heating in a furnace. Samples were produced with five-layer/cycle coating and ten layer/cycle coating.

## ***3.8.3 Materials Characterization***

The quality of the LbL-self-assembled and SILAR coated cerium oxide films were analyzed using an EXCALAB-250Xi X-ray photoelectron spectrometer (XPS) and UV-vis spectrometer. XPS was operated at room temperature in ultra-high vacuum chamber (below 8x10−9 mbar) using a monochromatic Al-Kα radiation source, operating at a power of 300 W (15 kV, 20 mA). The spot size of the beam was 650 µm. C 1s peak at 284.6 eV was used as a reference for calibration. Avantage Peakfit® software was used to deconvolute XPS spectra. Gaussian fittings were used throughout with a ‘smart’ background fitting to determine the measurement baselines for each sample. For reference XPS-simplified spectra from the Thermo Scientific website was used to compare against the obtained spectra as well as comparisons to literature values. Veeco Dimension 3100 system was used to perform Atomic force microscopy (AFM) scans to see surface morphologies, 2 µm \* 2 µm and 5 µm \* 5 µm area was scanned in tapping mode with 512 lines per scan. LbL coated films were subjected to UV-vis analysis to find the cerium oxide absorbance peak.

**4. Results and Discussion**

Due to the physical nature of the stepper motor’s governance over position the device is highly accurate. Every pulse of the coils moves the rotor 1/200th of a revolution or 1.8°±5%. The ±5% error in the individual step precision is not compounding when the motor rotates a full revolution because the amount of steps per revolution is fixed by the teeth in the motor's rotator. Due to the threading of the LEAD screw, every rotation moves the sample holder 8mm. Therefore 1 step moves the sample holder 0.04mm±0.002mm. So small, one step is imperceivable by the human eye. The max torque of the stepper motor is 1.1 N\*m and incorporated with the LEAD screw provides a max force on the /gantry plate of 115N or 26 pounds for both axes. The vertical axis linear actuator is approximately 2.7kg and applies about 26.75N of force to the device in the direction of gravity leaving 88.25N to move the sample vertically. Although the maximum mass of the sample could be 9kgs this is far greater than the total weight of the samples used in our experiments (<30gs coated) and would require the device to move as slow as possible.

Difficulty was had in improving the sensing capability of the device. The optical distance sensor used to detect beakers under the device failed to be effective due to the color and reflective properties of the materials it was intended to sense in contrast to the surrounding environment. In the place of an optical sensor, an ultrasonic sound sensor could be used to better detect objects regardless of their surface optical properties. This sensor uses a technique like echo-location to detect objects and is much better suited for clear objects like a glass beaker filled with aqueous solutions, water, or objects with light absorptive and diffusive properties, such as a matte black countertop.

Careful consideration must be taken when adding hardware components and related functionalities to the dipping instrument. Additional sensors must be orientated correctly to function properly and placed with enough clearance as to not obstruct the dipping process. Wires must be properly placed to avoid entanglement or contact with experimental materials. Attempting to simplify the operation of the device with the addition of a user interface on a computer or phone would produce the greatest increase in complexity: leading to an increased need for testing and, limiting the scope of the device's capabilities. In its simplest form without such front-end software, the dipping device controlled directly with Arduino code allows the most versatility in terms of movement control for experiment designs of arbitrary complexity. Distances can be calculated with respect to the 8 mm distance per full rotation of the gantry plates in the stepper motor. With 200 steps/revolution and a customizable micro-step feature, the desired traversable distances can be converted to micro steps with basic arithmetic.

Upgrades to the device can improve its capacity, autonomy and broaden the use cases but come at the cost of increased complexity of the program and physical system. A relatively simple upgrade would be to add a third dimension, or axis, of movement. This greatly increases the beaker capacity of the device multiple times over and could be controlled in a similar manner to the standard horizontal and vertical movement but would require two linear actuators for stability. An enclosure could be added to contain fumes or maintain environmental effects. Nozzles for spray applications of liquids to the sample and the automated valves to automate the timing could effectively turn this into a hybrid dip and spray coating device.

Sensors for beaker detection or errors in the dipping process along with video monitoring can be incorporated with the Arduino microcontroller as well as the Python programming language. These additions could be used in tandem with a cell phone sim card to send notifications via text message to the operator. Atmospheric sensors can easily be attached to the device and wired through the Arduino. Their data would then be stored via a file created with python to be used to document the environmental conditions during the experiment and determine the effects on the solutions, reactions, and layer quality.

Upgrading the device's microcontroller from Arduino to a Raspberry Pi like device would provide more memory and processing power but creates another programming layer on top of Arduino. This upgrade would remove the limitation of needing equidistant spacing between beakers due to the current limitation on number variables stored in the Arduino microcontroller. This would also allow for data to be processed within the microcontroller enabling faster data processing and reactions by the system.

The techniques used for nanoparticles epitaxial layer coating usually requires sophisticated equipment, inert atmosphere, high vacuum, and expensive precursors. Dip-coating is a well-known method used to produce LbL coatings on different substrates. However, it has certain drawbacks such as limited maximum sample size, long processing times, and variation in coating character due to imprecisions between depositions. To overcome these drawbacks, an Arduino-controlled automatic instrument was fabricated, at low cost, for multi-functional nanoparticles/polymer as well as nanoparticle coating for biomedical applications. The nanoparticles- polyelectrolyte multilayer coating can be grown on larger substrates by the Arduino-controlled instrument with less manpower. The substrate was dipped into dispersions of polyelectrolytes of alternating charge, with nanoparticles, to produce a uniform coating.

**4.1 LbL assembly**

Fig. 6a and b shows the layer-by-layer coated thin film and the UV-vis spectrum of naked glass slide, chi/PAA, and chi/PAA along with cerium oxide thin film. An absorption peak is observed at 298 nm due to CNPs embedded into Chi/PAA film. The chitosan/PAA along with CNPs coated on glass slide is confirmed by UV analysis (Fig. 6b). LbL grown films were further analyzed using XPS to confirm the presence of coating materials (Fig. 6c). The C1s envelope in Fig. 6c shows the multiple peaks of vibrational groups O-C=O (288.50 eV), C-O-C (286.62 eV), C-C/C=C, C=O (284.73 ev), and C-N (285.67 eV) which are mainly from the poly (acrylic acid) and chitosan coating. Similarly, -NH3+ (401.44 eV), -NH2+ (397.31 eV), and O=C-N (399.40 eV) peaks are identified in N1s confirming the poly (acrylic acid) and chitosan coatings on glass substrate. The coated CeO2 nanoparticles are also identified through XPS analysis. The XPS spectra collected for the material shows a characteristic high fraction of Ce3+ states relative to Ce4+. This information is obtained through fitting of the spectra to individual doublet peaks particular to each cerium redox state (i.e. u0, v0, u’, and v’ for Ce3+; u, v, u’’, v’’, u’’’, v’’’ for Ce4+). The relative amounts of each are calculated (using the integrated peak intensities for peaks related to both states determined through fitting and deconvolution, as detailed in ref23, 24. In most studies in literature the Ce3+ content is represented in ratio as the Ce3+/Ce4+ value as a figure of merit or practically as a reactivity index. By the current method, a value of 1.53 is determined (or 60.6% Ce3+ and 39.4% Ce4+). This value is especially high for a cerium oxide nanomaterial formulation suggesting a particularly high presence of reduced state cerium near the surface of the material important for antioxidant application. In aggregate, these results revealed that the chitosan, poly (acrylic acid) and CeO2 nanoparticles were successfully coated on the glass substrate through the Arduino controlled LbL coating device. Similarly, various nanoparticles (gold, silver, graphene, titanium oxide etc.) mix with suitable polymer electrolytes (heparin, sodium alginate, chondroitin sulphate etc.) and produce a better coating on the substrate.

**4.2 SILAR coating**

SILAR: Successive ionic layer adsorption and reaction; as evident by their name, this technique involves successive adsorption of precursors and oxidizers generally followed by oxidation on the surface to deposit the intended materials25-28. Reaction on the surface to form a new phase is the feature that separates SILAR from the LBL technique. LBL technique also involves successive layer deposition but usually doesn't involve any surface reaction to form a new phase*.* In our case, ceria was the desired material. Thin-film ceria coating has been utilized for various applications, and various techniques have been employed for the purpose (e.g. ALD, CVD, PVD). AFM (atomic force microscopy) has been used for thin-film surface characterization, and surface roughness estimated from the AFM scans can be used as a measure of the quality of films. The measurement essentially elucidates the uniformity and conformity of analyzed films. AFM deposited ceria films have been reported to have a surface roughness of 1.72 and 8.13 nm depending on process temperature29. SILAR ceria coated glass slides were subjected to AFM (fig. 7) and evidence observable grain growth from 5-layer samples (fig. 7A) to 10-layer samples (fig. 7B). Estimated roughness (rms) of the 5-layer sample was approximately 3 nm and ten layers samples were approximately 7 nm, indicating relatively uniform deposition of ceria layers and confirming the efficacy of layer-by-layer ceria coating through the facile SILAR method. SILAR deposited ceria films serve as a facile alternative to traditional coating high vacuum-based coating methods (ALD, CVD, etc.), although they have better precision on layer thickness. However, it should be noted that synthesis has high throughput requirements and is ideal for applications which do not require extreme precision in layer thickness.

XPS was also performed to confirm the formation and relative growth of the ceria layer. Fig. 8A and B shows a Ce3d scan with peaks uniquely associated with Ce3+ and Ce4+ oxidation states, characteristic of the mixed-valence presenting in cerium oxides. As evident from the spectra, the concentration of Ce4+ (Ce3d5/2 : 882 and 888.3; Ce3d3/2: 897 eV, 900.3 eV, 906.7 eV, satellite peak: 916 eV) is greater than Ce3+ ( Ce3d5/2 : 879.8 eV, 884.6 eV; Ce3d3/2: 895.7 eV and 903 eV) oxidation states, which is typical for cerium oxide. Further, the Ce3+/Ce4+ ratio in 5-layer and 10-layer samples were 0.81 and 0.297 respectively, signifying decreasing Ce3+ concentration with increasing total coating layers. It also confirms the formation of cerium oxide thin films (Fig. 8 A and B). The atomic ratio of cerium to oxygen, determined from XPS survey spectra ~0.24 and ~0.49 in 5-layer and 10-layer samples; less than the ideal ratio of 0.5 (Fig. 8C and D). The wide difference in this metric, between samples, suggests a significant difference in oxygen vacancy densities, as supported by the greater Ce3+/Ce4+ ratio determined for the 5-layer sample. By using sodium hydroxide to force hydrolysis, there is a possibility of sodium contamination, making the estimation of sodium in the coating essential. The sodium to oxygen ratio was ~ 0.016, signifying trace amount and relative phase purity for the sample.

SILAR deposited Ceria films serve as a facile alternative to traditional high vacuum-based coating methods (ALD, CVD, etc.), although they have better precision on layer thickness. Study of coating thickness and linearity with respect to cycle number, the impact of further decrement of percussor concentrations on it are part of our future work also out of scope of our current discussion, which is more scientific instrument oriented.

**5. Conclusions**

Overall, the results show that this dip coating device is capable of producing thin films via layer-by-layer assembly and SILAR methods at a fraction of the cost of commercially available dipping devices. SILAR coating of nano ceria was achieved without any post processing heating at high temperatures. The same device could be used for other dipping functions enabled by the high mechanical precision and simple, customizable programming. Hundreds of hours have already been saved using this device to reliably create samples with 1-100 nano layers allowing for expedited research as staff work on other tasks. With reduced personnel hours needed and low device costs, creating coatings on complicated surfaces, SILAR reactions on substrates, and LbL films for drug delivery or self-healing surfaces can become more widely available for research and production anywhere there is electricity and a simple computer.

**Supplementary Material**

Please see supplementary material for the comprehensive materials lists, including costs and sources. It also contains detailed, yet simple to understand, examples of code from the controlling software along with comments for each line.

**Acknowledgments**

We would like to acknowledge partial support from NSF (National Science Foundation) (CBET: 2027489: RAPID COVID 19) and XPS measurements under the NSF MRI: ECCS: 1726636. KE acknowledge to UCF Preeminent Postdoctoral Program (P3) for the partial funding support. Biorender software (Biorender.com) was used to create illustrative diagram.

**Data availability statement**

The data that supports the findings of this study are available within the article and its supplementary material.

**Conflicts of Interest**

The authors declare no conflict of interest.

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**List of tables**

**Table 1.** List of parts used in the construction of the device with sources and costs. Website links are located in appendix 1. Part I.D.s on the left-hand side are referenced in this work.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Part**  **I.D.** | **Item** | **Cost** | **Source** | **#** | **Total Cost** |
| **1A** | C-Ceam Liner Actuator Bundle W/ Nema 23 -250 mm | $140.99 | OpenBuilds | 1 | $140.99 |
| **1B** | C-Ceam Liner Actuator Bundle W/ Nema 23 -1000 mm | $189.99 | OpenBuilds | 1 | $189.99 |
| **1C** | Assorted Parts List (mechanical) | $80.01 | OpenBuilds | 1 | $80.01 |
| **2A** | Arduino Microcontroller – Mega 2560 | $40.30 | Arduino | 1 | $40.30 |
| **2B** | Sparkfun Autodriver -L6470 | $38.95 | Sparkfun | 2 | $77.90 |
| **2C** | Power Supply Unit – LRS-100-24 | $18.13 | Allied Electronics | 1 | $18.13 |
| **2D** | Assorted Parts List (electrical) | $39.10 | Sparkfun | 1 | $39.10 |
| **3A** | Laser Diode -5mW/650 nM | $5.95 | Adafruit | 1 | $5.95 |
| **4A** | Brass Solenoid Valve 24V DC -5LU11 | $148.05 | Granger Industrial | 1 | $148.05 |
| **4B** | MOSFET Switch (Gas Valve Control) | $1.49 | RobotDyn | 1 | $1.49 |
| **4C** | Diode kit -IN4002 | $9.99 | Amazon | 1 | $9.99 |
|  | **3D Printing** |  |  |  |  |
| **5A** | Prusa MK3S | $749.00 | Prusa |  |  |
| **5B** | PLA - 0.15 Silver 1kg - Prusa | $34.99 | Prusa | 1 | $34.99 |
|  | **Software** |  |  |  |  |
| **6A** | Arduino IDE | $0.00 | Arduino |  |  |
| **6B** | Visual Studio Code | $0.00 | VisualStudio |  |  |
| **6C** | AutoCAD 2020 Student Version | $0.00 | AutoDesk |  |  |
| **6D** | PrusaSlicer | $0.00 | Prusa |  |  |
|  |  |  |  |  | $786.89 |

List of figures:

**Fig. 1**(a) Depiction of the control system for motion of the device showing the program hierarchy for the GUI, that communicates both ways with the Arduino which then sends commands to the autodrivers thereby turning the motors and moving the sample and (b) The stepper motors (1A and 1B) are connected to the L6470 autodrivers (2B) and to the 24DC power supply(2C). The Arduino Mega 2560 (2A) is the logic center of the system connected to the autodrivers, limit switches (1C), laser diode (3A), and solenoid valve(4A) via the MOSFET switch (4B).

**Fig. 2 (a**) The GUI starts with unique variables needing to be defined once. Continuing downward, variables are defined for each beaker position. At the bottom are buttons for functions that physically move the device and (b) The structure of the Python code starts with initiating libraries of code and defining variables which will be used throughout the program. The Tkinter class that defines the GUI is coded in the linear order shown, starting with initiating class variables down to defining the interactive functions. Serial connection monitoring is done via the check Buffer () function (Appendix 3b) followed by running the “mainloop” which cycles through the code updating the GUI as needed.

**Fig. 3** 3D printed samples holders. (a) The bottom of the sample holder showing the positioning of the tapered substrate inserts. Tapering inside the insert enables accommodation of various thicknesses of substrate according to the tolerances specified by the substrate manufacturer. (b) The laser is slid into its respective holder giving clearance for the sample holder to be positioned at any of the five pin slots (c) A color coded image from PrusaSlicer V2.2.0 showing the 3D printer nozzle path for the creation of the sample-holder attachment point. Red is the infill. Yellow and orange are the inner and outer walls respectively. Green shows where supports will be created to allow for surfaces of the model that are horizontal to the build plate but do not rest directly on the plate itself.

**Fig.4** The dipping device during a multiple tri-layer coating. Stepper motors can be seen on the left connected to their respective lead screws and attached via the gantry plate. The LbL coating process occurs during steps 1, 3, and 5 with 2, 4, 6 and 7 consisting of washing with deionized water.

**Fig.5**: Schematic diagram illustrating the SILAR (Successive Ionic Layer Adsorption and reaction) coating of ceria on the glass substrate. One cycle of the process contains dipping of the sample in ceria precursor (cerium nitrate 0.0057 M) followed by washing step (water) then sodium hydroxide (as oxidizer) again followed by water, the process is repeated for desired number of cycles. Samples obtained from the SILAR process again get subjected to post-process washing to remove residual solution components (e.g., counter-ions, reactants).

**Fig. 6(a)** The polyelectrolytes of chitosan and poly (acrylic acid) and cerium oxide nanoparticle used for layer-by-layer coating on glass at room temperature. (a) shows the glass etched with 30% sulfuric acid at 70 ºC for 3 h and then washed with running deionized water (control), 20 layer pair of chitosan and poly(acrylic acid) coated on acid etched glass (Chi/PAA) and 20 layer pair of chitosan with cerium oxide/PAA coated on acid etched glass (CNPs-Chi/PAA). (b) UV-vis analysis of polymers along with CNPs coated on glass by LbL technique. The absorbance peak at 298 nm observed on CNPs-Chi/PAA film which indicates the CNPs coated along with polyelectrolytes and further (c) The carbon (C 1s) and nitrogen (N 1s) of poly (acrylic acid) and chitosan shows the functional group present in the coating (functional groups are indicated through the arrows) as well as Ce3d indicates the presence of CeO2 nanoparticle in the coating.

**Fig. 7** AFM images of ceria thin film coated by SILAR technique using LbL method; (A) shows the AFM scan of 5 SILAR layer/cycles deposited on the glass substrate, scan area is 3 µm \* 3 µm with height scale 1.4 to 37.6 nm; (B) shows the AFM scan of 10 SILAR layer/cycles deposited on the glass substrate, scan area is 5 \* 5 µm with height scale 7 to 119 nm; Ceria grain growth can be seen in the 10-layer coated sample with respect to the 5 layer sample. (Scan size – 2 µm x 2 µm)

**Fig. 8** A and B shows the survey spectrum with peaks corresponding to specific elements noted ten-layers and five-layers SILAR ceria coated samples, cerium and oxygen are in the majority, with carbon noted from adventitious sources; C and D shows Ce3d XPS spectra of ten-layer and five-layer SILAR ceria coated sample with peaks corresponding to Ce3+ and Ce4+ oxidation states; C shows relevant atomic ratios from the survey spectrum of the samples with Ce/O ratio suggesting non-stoichiometry/cerium reduction (0.49 for 10-layer sample which is slightly less than the ideal atomic ratio of 0.5: suggesting oxygen vacancies and 0.24 for five layer sample suggesting more oxygen vacancies), it also shows the Ce3+/Ce4+ ratio estimated from Ce3d scans of respective samples, it decrease from 0.81 in 5-layer to 0.297 in 10-layer samples signifying a decrease in Ce3+ concentration with increase in the thickness.

Fig. 1

Diagram, schematic

Description automatically generated

Diagram

Description automatically generatedFig. 2

Fig. 3

Graphical user interface

Description automatically generated

Fig. 4

Graphical user interface

Description automatically generated

Fig. 5

Graphical user interface, diagram, application

Description automatically generated

Fig. 6

A picture containing chart

Description automatically generated

Fig. 7



Fig. 8

Graphical user interface

Description automatically generated