Lab 10 – Layer by Layer (LBL) Deposition of Gold Nanoparticles

Pre-Lab Reading:

Layer-by-layer (LBL) deposition is a fabrication method used in both industry and nanotechnology research to create thin films with control over thickness, composition, and functionality. This technique involves the sequential adsorption of materials such as nanoparticles or other functional species onto a substrate. Each deposition cycle adds a controlled amount of material, usually in the order of nanometers, which allows for fine control of a deposited film.

In research settings, LBL deposition is used to build multilayered **nanostructures** for applications in drug delivery, biosensing, photovoltaics, and energy storage. For example, researchers can deposit films with specific materials to build nanometer-scale structures with tailored properties for various applications. While in industrial applications, LBL is valued for its ability to **functionalize** surfaces without the need for complex lithography or etching. One use is in barrier coatings for packaging, where multilayer nano-coatings improve oxygen or moisture resistance.

The main advantage of LBL deposition is its atomic or molecular-level control over film architecture, which allows tuning of film thickness, composition gradients, and interface properties. This is particularly important in biosensor development, where sensitive detection layers can be engineered with nanometer-scale precision. For example, alternating layers of enzymes and conductive polymers can be assembled to optimize signal transduction and specificity. Similarly, in photovoltaic devices, LBL assembly of quantum dots or organic semiconductors can enhance light absorption and charge separation.

Despite its advantages, LBL is not as widely adopted in high-volume semiconductor manufacturing due to relatively low throughput compared to methods like chemical vapor deposition (CVD) or physical vapor deposition (PVD). However, it remains a critical technique in applications where precision and material versatility outweigh throughput concerns. Hybrid manufacturing approaches have also emerged, where LBL is integrated with printing or lithographic methods to pattern multilayer nanostructures over large areas, bridging the gap between laboratory-scale fabrication and scalable industrial processes.

Objective:

The objective of this lab is for students to learn the process of layer-by-layer deposition through electrostatic self-assembly. Students will prepare gold colloidal nanoparticles and then deposit gold nanoparticles on the surface of a glass substrate to form a thin film. The color change of the thin film will be observed with increasing thickness of the film by the students. Eventually, students will see the color of the film become metallic gold.

Background:

Self-assembly (SA) is an effective method for constructing nanoscale layers and coatings on various substrates. Self-assembled monolayers (SAMs) are essential for modifying the interfacial properties of substrates, enabling the development of materials with tailored characteristics for different applications. The strong interactions within SAMs arise from the covalent bonds formed between the adsorbed molecules and the substrate. A common example is the self-assembly of alkanethiols on gold surfaces, which results in an ordered, structured layer.

Electrostatic self-assembly (ESA) is a variant of the covalent bond-based self-assembly (SA) method. ESA was developed by Decher in the early 1990s. This technique relies on electrostatic absorption, where a charged surface is immersed in a solution containing a polymer with oppositely charged functional groups. The surface's charge is then reversed after rinsing by placing the charged substrate back into a solution with an oppositely charged polymer. This process can be repeated until the desired number of layers is achieved. ESA enables the rapid and straightforward creation of multilayered structures. Since this method is purely based on electrostatic interactions, it does not require the close molecular proximity or affinity necessary for chemical bond formation, resulting in layers that are less organized and exhibit higher disorder. Despite this, ESA layers are very stable. Electrostatic repulsion prevents the adsorption of more than one polyelectrolyte layer with the same charge, leading to the formation of a single polymeric layer at each step. However, by alternating the adsorption of oppositely charged polymers, the construction of a multilayered structure is easily achievable. The thickness of these layers is directly proportional to the number of layers. ESA layers are synthetically much easier to produce than comparable layers using the SA method, and they can be applied to any surface with compatible charges between the polymers. As a result, it has been widely used for layer-by-layer (LBL) assembly in various nanoscale applications.

In this lab, students will use the ESA LBL method to deposit gold nanoparticles on the glass substrate. Poly(diallyldimethylammonium chloride) (PDDA) containing polycations was used along with gold NP for LBL assembly. The schematic representation of a bilayer formation of LBL is shown in *Figure 10.1*. The glass substrate is prepared with isopropanol and 1 M NaOH. After the preparation, the surface charge is negative. After immersing the glass slide in PDDA solution, the surface charge changes to positive. After switching to the gold NP solution, the surface charge changes back to negative. Gold nanoparticles were used in this study due to their interesting optical properties. The gold colloid was first discovered by Michael Faraday in the mid-1850s. Faraday was trying to create gold slides thin enough to be transparent, to study the properties of light and matter. While washing the gold with chemicals, he noticed a faint ruby-colored fluid. When Faraday shined a beam of light through the fluid, he noted in his journal, "The cone was well defined in the fluid by the illuminated particles." He realized that this effect was due to suspended gold particles in the fluid, which were too small to be seen with the scientific instruments of the time but scattered light to the side. This phenomenon is now known as the Faraday-Tyndall effect. The color of the gold colloid can vary depending on the size of the nanoparticles, which can be observed by students during the synthesis of gold colloid when $HAuCl_4$ is reduced by sodium citrate in boiling water. The negatively charged citrate ions adsorb onto the surface of the gold nanoparticles, and the resulting electrostatic repulsion helps keep the gold nanoparticles stable. The color of the thin layer of gold deposited on the glass substrate is determined by the thickness of the film and the thickness of the film can be controlled with number of PDDA/AuNP bilayers deposited. For visual observation, higher concentrations of gold colloid are used in the experiment. A diluted gold colloid can be used to achieve an even thinner deposition. The time immersed in the gold colloid is another factor that affects the growth of the film.

Experiment:

SAFETY DISCLOSURE: This lab contains the use of hydrogen tetrchloroaurate solution which is corrosive to skin and can cause severe eye damage. It is recommended that the instructor prepares the solution for students to use. Also, sodium hydroxide is

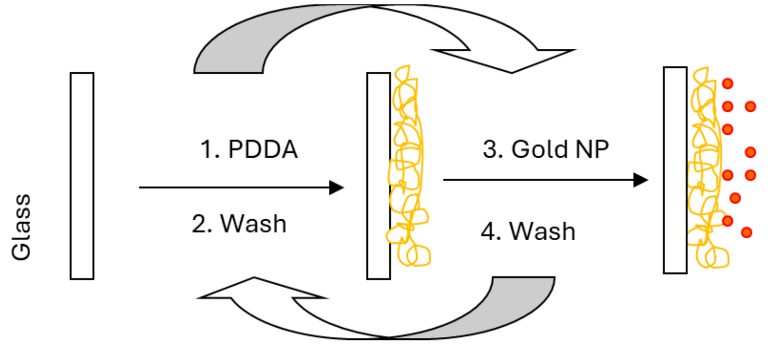

Figure 10.1: LBL formation of glass/PDDA/AuNP.

a strong base and is corrosive. For students' safety and protection, personal protective equipment (PPE) is required for this lab. PPE should include gloves, chemical splash goggles and aprons. It is recommended the lab be conducted under the fume hood.

Required Materials:

1. Microscope slides
    a. Link
2. 99% Isopropanol in squirt bottle
    a. Link
3. 1M Sodium Hydroxide
    a. Link
4. 1.0 mM hydrogen tetrachloroaurate
    a. Link The solid is hygroscopic so purchase $HAuCl_4{:}3H_2O$ (Aldrich 244597 or 520918) in 1.0 g quantities and use the entire bottle. Dissolve 1.0 g $HAuCl_4{:}3H_2O$ in 250 mL distilled water to make a 10.0 mM stock solution of gold(III) ions that can be kept for years if stored in a brown bottle. Dilute 25 mL of stock to 250 mL to make the 1.0 mM concentration for this experiment.
5. 1% Trisodium citrate solution
    a. Dissolve 0.5 grams of trisodium citrate dihydrate, $Na_3C_6H_5O_7{\cdot}2H_2O$ in 50mL distilled water. Trisodium citrate dihydrate can be purchased through Link
6. 1 wt% PDDA solution
    a. Weigh 2.86g of 35 wt% PDDA in a small beaker. Add 20mL distilled water into the beaker to dilute the PDDA solution. Transfer the solution to a 100mL volumetric flask and add distilled water until the mark. Shake the solution before use. 35 wt% PDDA can be purchased through this link.
7. 10 mL graduated cylinder
8. 50 mL beaker
9. Three 30 mL beaker
10. Stirring hot plate
    a. Link
11. A magnetic stir bar
    a. Link
12. Sharpie for labeling glassware

Step 1: Prepare the microscope glass.

Rinse both sides of microscope glass with isopropanol, and then rinse with distilled water. Dry the glass slide. Dispense 25 mL of 1M NaOH into a 30 mL beaker. Soak the glass slide in the beaker for about half an hour. During the soaking period proceed step 2.

Step 2: Gold NP preparation with sodium citrate.

Measure 20 mL of 1.0 mM $HAuCl_4$ into a 50 mL beaker or Erlenmeyer flask. Place the beaker on a stirring hot plate. Add a magnetic stir bar and heat the solution until it reaches a vigorous boil. Once boiling, quickly add 2 mL of a 1% trisodium citrate dihydrate solution ($Na_3C_6H_5O_7{\cdot}2H_2O$) to the boiling mixture. The gold solution will gradually form as the citrate reduces the gold(III). Remove the mixture from heat once it turns deep red or after 10 minutes, whichever comes first. Let it cool before use. Record the color change of the solution in the beaker.

Table 10.1: Data from Step 2

Color of $HAuCl_4$ solution (before reaction)	Color immediately after the addition of citrate	Color of the final gold colloid	Any intermediate colors? What color?

Step 3: LBL assembly on glass slides.

Label one 30 mL beaker with 1% PDDA and dispense 25 mL of 1% PDDA into the beaker. Label another 30 mL beaker with Gold NP and pour the cooled gold colloid solution into the beaker. Lift the glass slide from the 1M NaOH solution, rinse the glass slide with distilled water. Dry the glass slide with air. Place the glass slide in 1% PDDA for 10 minutes. Discard the NaOH solution into a waste container and clean the beaker. Label the cleaned beaker with DI water and place 25 mL distilled water into the beaker. This beaker will be used for rinsing between depositions. After 10 minutes in 1% PDDA solution, lift the glass slide and place in the DI water beaker for a few minutes, dry the glass slide after. Then place the glass slide in gold NP beaker for another 10 minutes. Clean with DI water and dry the glass slide after. This is considered the first layer of the gold deposition. Repeat the process by dipping in 1% PDDA and gold NP solution alternately with washing and drying in between. The experimental set up is shown in *Figure 10.2*. The rinsing and drying are important steps as the excess PDDA will cause the coagulation of the gold colloid solution. Depending on the length of the laboratory hours, deposit as many layers as possible. After the last dip in 1% PDDA solution, rinse and dry the glass slide and leave the glass slide in gold NP solution. Students can come to make observations on the second day or during the next scheduled lab period. Record the color of the gold film on glass after each bilayer deposition.

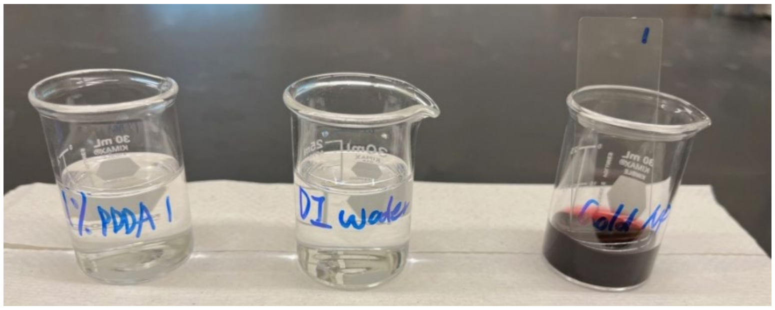

Figure 10.2: Experiment setup for LBL formation of Glass/(PDDA/AuNP)

Table 10.2: Data from Step 3

Number of bilayers	**1**	**2**	**3**	**4**
Time in PDDA solution (min)				
Time in gold colloid (min)				
Color of the film				

Questions:

1. What is the color of the thin film after depositing the 1st bilayer? Is this the same color as the gold colloid? If different, explain why the gold nanoparticles changes color after deposition.
2. What color change was observed when more bilayers were deposited on the glass substrate? Why is the color of the film not golden?
3. List factors that affect the gold deposition process? How do they affect the growth of gold film on the substrate?
4. How many bilayers were deposited until a noticeable metallic gold film showed on the substrate? Is the film uniform?
5. The LBL assembly was performed in water. Will a change in pH affect the process?
6. How is self assembly used in research and industry? Research and cite a source.
7. Explain the LBL process in your own words.
8. What are some of the limitations of the LBL deposition process?
9. What are some of the applications of products created by the LBL process?
10. What are some other ways that LBL deposition is done? Research and cite a source.