Self-Assembled Antireflective Coatings Using

Silica and Titania Nanoparticles

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Abstract

Antireflective coatings have a wide range of applications, from eyeglass and camera lenses to solar panels, and from microscope lenses and optoelectronic devices to skyscraper windows. It is well known that an uncoated glass substrate transmits approximately 92% of the light incident on it and reflects back approximately 8%. Our research involves the fabrication of antireflective coatings which transmit light in excess of 92% and hence reduce the amount of light that is reflected from the surface of the glass substrate. Our research also focuses on the efficient, cost-effective production of these anti-reflective coatings. Our study examines several factors that affect the quality of antireflective coatings created by the ionic self-assembly of multilayers (ISAM) of silica (SiO$_2$) and/or titania (TiO$_2$) nanoparticles with poly(diallyldimethylammonium chloride) (PDDA) polycation on glass substrates. We use factorial design in order to design our experiments, which enables us to investigate the effects of multiple factors (such as the molarity and pH of the nanoparticle solutions, the size of the nanoparticles and the number of nanoparticle-polycation bilayers) on the optical properties of the films simultaneously. The first order effects of these factors, as well as their interactions on the reflectance, transmittance, and uniformity of the coatings are reported. We find that a number of different factor-level combinations exhibit transmittance values in excess of 96%, well above that of an untreated slide and comparable to commercial coatings.
Background and Introduction

*Thin-film interference*

As a young child you might have played with soap bubbles and noticed delightful rainbow colors twisting and twirling in them. Rather less delightfully, you might have also noticed them at a gas station in puddles of water, an indication of gasoline spills polluting the water. These are examples of thin-film interference occurring in nature. Fine lenses for cameras, microscopes, watches and binoculars, to name just a few, have transparent coatings on their optical surfaces. For example, the four images below illustrate some common uses of thin film coatings.

![Figure 1. Camera Lens](image1)

![Figure 2. Binocular Lens](image2)

![Figure 3. Skyscraper window panes](image3)

![Figure 4. Soap bubbles](image4)

Constructive and destructive interference of light waves is the reason why thin films, such as soap bubbles, show the colorful patterns and why lens coatings appear to have a particular color. Light waves reflecting off the top surface of the film interfere with waves reflecting off the
bottom surface. If the reflected waves from the two surfaces are in phase with each other constructive interference results and if the two reflected waves from the two interfaces are $\pi$ radians out of phase then destructive interference takes place. Aside from a path difference, there is another way to introduce a phase difference between the two waves. When a wave is reflected, a phase change of $\pi$ radians may occur for the reflected wave. Experiments indicate two circumstances which lead to such phase changes.

(i). If the incident light reflects off the surface of a conductor, the situation is analogous to the reflection of a wave traveling through a rope off the fixed end of the rope. In this case, the reflected wave experiences a phase change of $\pi$ radians. [5].

(ii). A phase change of $\pi$ radians also occurs if the incident wave reflects off an optically more dense material, i.e., a medium with a higher index of refraction ($n_2 > n_1$). This situation is analogous to a rope pulse reflecting from a section of rope with a greater mass per unit length than that of the incident pulse.

If the index of refraction of the second medium is less than the one of the first medium ($n_2 < n_1$), no phase change occurs in the reflected wave. [5].
When light is incident on the interface between two transparent media, some light is reflected at
the interface while the rest of the light passes through. The amount of light that is reflected
depends on a number of factors such as the indices of refraction of the two media and the angle
of incidence. For light incident along the normal to the surface, approximately 4% of the light is
reflected back from each interface [5]. Therefore, a total of about 8% of the light will be
reflected from the two interfaces while approximately 92% of the light will be transmitted
through the glass substrate. The illustrations below show agreement between these theoretical
values and the measured values of the transmittance and reflectance of an uncoated glass slide.
The measurements were taken with a Filmetrics F20 Thin-Film Analyzer.

Figure 7. Transmittance of an untreated glass microscope slide
Figure 8. Reflectance of an untreated glass microscope slide

Suppose monochromatic light is incident on a thin film that separates two other transparent media as shown in the figure below.

![Diagram showing light incident on thin film](image)

Figure 9. Light incident along the normal to a thin film separating two other transparent media [5]
Some light is reflected from the first interface while some light is reflected from the second interface. It is the interference of these two reflected waves that we are interested in. To determine the nature of the interference of the reflected waves, we need to consider two factors that contribute to their phase difference:

(i). A path difference
(ii). Phase changes from reflection

Path difference
The wave reflected from the lower interface travels an additional distance $2d$ before it is superimposed and interferes with the wave reflected from the top interface, where $d$ is the thickness of the film. This path difference corresponds to a phase difference (in radians) of

$$\delta_{path} = \frac{2d}{\lambda_{film}} (2\pi)$$

where

$$\lambda_{film} = \frac{\lambda_{vacuum}}{n_{film}}$$

Phase changes upon reflection
There are three situations that may arise:

(i). Neither reflected wave experiences a phase change upon reflection.
(ii). Both reflected waves experience a phase change upon reflection.
(iii). Only one of the two waves experience a phase change upon reflection.

Since the same phase shift has occurred for both reflected waves in either of the first two cases, the phase changes upon reflection thus are irrelevant in assessing the phase difference of the reflected waves. For either of these cases, the interference of the two waves is determined solely from the path difference between the two reflected waves [5].

If the thickness of the film is such that the phase difference arising from the path difference is a multiple of $2\pi$, the interference of the two waves is completely constructive, that is, the amplitudes of the waves add up.
\[
\frac{2d}{\lambda_{\text{film}}} (2\pi) = m(2\pi) \\
\]
\(m = \text{integer (Constructive Interference)}\)

If the thickness of the film is such that the resulting phase difference is an odd multiple of \(\pi\) rad, the resulting interference of the two reflected waves is completely destructive. From above, if \(m\) is an integer, then \(2m+1\) is an odd integer. This condition will lead to destructive interference.

\[
\frac{2d}{\lambda_{\text{film}}} (2\pi) = m(2\pi + 1) \\
\]
\(m = \text{integer (Destructive Interference)}\)

The third case occurs when only one of the reflected waves experiences a phase change of \(\pi\) rad upon reflection; it does not matter which of the two waves experiences the phase change. The important thing is that one reflected wave does and the other does not. If this is the case then the conditions for constructive and destructive interference are reversed.

\[
\frac{2d}{\lambda_{\text{film}}} (2\pi) = m(2\pi) \\
\]
\(m = \text{integer (Destructive interference)}\)

\[
\frac{2d}{\lambda_{\text{film}}} (2\pi) = m(2\pi + 1) \\
\]
\(m = \text{integer (Constructive interference)}\)

If the path difference implies a phase difference between the waves of a multiple of \(2\pi\), mistakenly leading us to think that the waves are in phase and will result in constructive interference, the phase change upon reflection of one but not the other wave means that the two will be out of phase and destructive interference will result. On the other hand, if the path difference implies a phase difference of an odd multiple of \(\pi\) radians, leading us to think that the waves are out phase and destructive interference will occur, the phase change upon reflection of one wave and not the other must mean that the two waves are in phase and constructive interference will occur [5].
What we desire for antireflective coatings is destructive interference of the two reflected waves. Thus, thin-film destructive interference is the principle behind coating optical surfaces such as lenses to minimize reflections and allow more light to be transmitted. The purpose of our experiments is to produce thin-films which have properties that will lead to destructive interference of the waves reflected from the interfaces and thus known as anti-reflective coatings.

**Rayleigh scattering**

So far we have stated that approximately 92% of the incident light is transmitted and roughly 8% of it is reflected from the surface of an untreated glass substrate. This may mistakenly lead the reader to believe that the 100% of the incoming light rays have been accounted for. However, this is essentially not the case as some fraction of the light is scattered at the interface with the second medium. This scattered light is essentially lost and is therefore not transmitted, thus harming the quality of the anti-reflective coatings.

Imagine a narrow beam of sunlight having a broad range of frequencies propagating through empty space. As it progresses the beam spreads out very slightly, but apart from that there is not much scattering nor does the light diminish in any way [8]. The atmosphere is a mixture of gas molecules (approximately 78% nitrogen and 21% oxygen) and water vapor. Argon gas, water droplets and ice crystals are also present, as well as small amounts of other gasses and particulates like dust, soot and ashes, pollen and salt from the oceans. Each molecule behaves as a little oscillator whose electron cloud can be driven into a ground-state vibration by an incoming photon. Immediately upon being set vibrating, the molecule initiates the re-emission of light. A photon is absorbed and without delay another photon of the same frequency (and wavelength) is emitted; the light is *elastically scattered*. Since the molecules are randomly oriented, the photons are scattered out every which way [8]. The closer the frequencies of the incoming photons are to the resonance frequencies of the oscillating molecules suspended in the atmosphere, the greater the scattering. As light traverses through the atmosphere, most of the longer wavelengths pass straight through. As such little of the red, orange and yellow light is affected by the air.
However, much of the shorter wavelengths (violet and blue) is absorbed by the suspended molecules and radiated in different directions. Sunlight, not having very much violet in the first place, will be richer in blue. That, in part, is why the sky is blue. This phenomenon is known as Rayleigh scattering after the British physicist Lord Rayleigh who studied scattered sunlight in terms of molecular oscillators. He concluded that the intensity of the scattered light was proportional to $1/\lambda^4$, where lambda is the wavelength of the incident light [8]. The illustration below depicts the phenomenon of Rayleigh scattering.

![Rayleigh scattering diagram](image)

Figure 10. Shorter wavelengths from the sunlight being absorbed and scattered randomly [9]

Since scattering has a significant effect on the amount of light being transmitted and influences the quality of our anti-reflective coatings, it becomes extremely important that we determine the percentage of light that is lost due to this process.
Why use nanoparticles to manufacture the thin films

The ability to enhance the transmittance of light and remove “ghost images” has attracted a lot of attention for anti-reflective (AR) coatings. Antireflective coatings have applications in photovoltaic and displaying devices and all kinds of optical devices. When the refractive index ($n_c$) of an ideal homogenous AR coating meets the condition of $n_c = \sqrt{n_a \cdot n_s}$, reflection will be suppressed at the wavelengths near four times the optical thickness of the coating. Here, $n_a$ and $n_s$ are the refractive indices of the air and the substrate respectively, and the optical thickness is defined as the product of the refractive index of the film and its physical thickness. For a glass substrate, similar to the one that we will be using for our purpose, for which the refractive index $n_s \approx 1.5$, the refractive index of the AR should be $n_c = \sqrt{(1.00)(1.50)} \approx 1.22$. However, natural materials with such low refractive index are either rare or expensive to obtain in thin film form. One of the easiest ways to obtain such a low refractive index is to introduce nanopores during thin-film fabrication [10]. This can be achieved through the use of nanoparticles in the fabrication of the AR coatings. As the number of nanopores is increased, a lower refractive index can be achieved. Some of the methods that have been used to incorporate the nanopores are plasma enhanced chemical vapor deposition, nanophase separation, chemical etching, UV or thermal – decomposition of porogen, sol – gel processes. Amongst these methods, the layer-by-layer (LBL) self-assembly has been the most efficient [10].

Layer-by-layer self-assembly of the thin-film coatings

In our manufacture of thin-film coatings we use a technique known as layer-by-layer (LBL) self-assembly. This technique involves depositing alternate layers of positively and negatively charged colloidal particles, such as a silica and alumina from solutions onto a smooth surface such as glass. By this means, films of controlled, uniform thickness can be built up. By using uniform colloidal particles like silica as a visible indicator film, the adsorption of invisibly small particles, polyvalent ions, surfactants and water soluble polymers can be observed. This also makes it possible to study the adsorption of colloidal particles from aqueous solution onto various surfaces [11]. In our experiments we used this technique to form alternating layers of
silica nanoparticles and the polycation poly(diallyldimethylammonium chloride) (PDDA) to fabricate AR coatings.

These SEM images [10] provide an example of LBL deposition of PDDA/SiO$_2$ nanoparticle multilayer films. It can be seen that with increasing deposition cycles (1, 3, 5, and 8 bilayers, respectively), the coverage of the SiO$_2$ nanoparticles increases dramatically. Layer-by-layer (LBL) self-assembly is a simple, but most importantly, a fairly inexpensive technique by which nanoparticles can be deposited on a substrate regardless of its shape, that is, planar or non-planar [12]. It also has other advantages such as allowing the fabrication of AR coatings with more precise thickness. LBL also allows other nanomaterials such as nanosheets and nanowires to be merged as a single material so that the unique properties of these materials can be manipulated to attain the desired properties of the coating [12]. An especially important industrial use of LBL is that it has led to the manufacture of nanotubes which play an important role in biomedical applications [12]. Its other applications include drug delivery systems, battery
electrolytes and thin membranes. In general, the LBL process is achieved by alternately exposing a substrate to positively and negatively charged particles as illustrated in Figure 12.

Figure 12. The setup for layer-by-layer deposition of the nanoparticles [12]

In LBL, steps 1–4 are repeated continuously until the desired numbers of “bilayers” are achieved. Each individual layer thickness and LBL growth depends upon various factors including the chemistry used, charge density, molecular weight, temperature, deposition time, the concentration and the pH of the species being deposited.
The forces that promote formation of LBL films include electrostatic interactions, ionic charge transfer, hydrogen bond, covalent attachment, biological attachment, biological recognition and hydrophobic interactions. In general, for the LBL assembly process, the common positively charged polyelectrolytes used are poly (allylaminehydrochloride) (PAH), poly(diallyldimethylammonium chloride) (PDDA) and polyethyleneimine (PEI). Once they are attached on the substrate, the net charge on the substrate surface becomes positive because of the adsorption of polyelectrolytes with positive charge. The films are consequently washed with pure (de-ionized) water; the aim of washing is to get rid of any extra reagents or remove loosely adsorbed polyelectrolytes. To subsequently grow the LBL further, the films are introduced with negatively charged polyelectrolytes such as silica and titania colloidal solutions. Other typical negatively charged polyelectrolytes include poly (acrylic acid) (PAA), poly (styrene sulfonate) (PSS), poly (vinyl sulfate), which leads to the reversal of the net charge on the substrate. With such cyclic depositions, one can achieve multilayer films on the substrates with desired thickness and structures [12].

For a clearer understanding of the technique, a specific example will be described. Starting with a clean, hydrophilic glass surface, which is siliceous and anionic in nature, the first step is to apply a layer of positively charged material which in our case is the PDDA solution. The excess solution is then rinsed off. At this stage there is no visible change in the appearance of the treated surface. The surface is then wetted with colloidal silica, supposedly consisting of uniform spherical particles, which has been adjusted to a certain pH with hydrochloric acid and sodium hydroxide as a strong base [11]. The excess solution is then rinsed off and the surface is allowed to dry. In reflected light a colored film of silica then appears on the area previously treated with the positively charged solution. On the other hand no film is visible on the untreated area. The negatively charged silica particles adhere only to the area of glass covered with positively charged solution and not to the negatively charged glass. Likewise another layer of positively charged solution may be applied to the now negatively charged surface achieved by the deposition of the silica (negative) nanoparticles followed by another layer of the silica nanoparticles. The excess of each solution is rinsed off before the next one is applied. In this way a uniform film of increasing thickness may be built up.
When a single layer of colloidal particles is adsorbed from an aqueous solution onto a smooth, solid surface of opposite ionic charge, no further adsorption occurs because the ionic charge on the surface is reversed and the remaining colloidal particles in solution are repelled and are later washed off during the rinsing process. By repeating the operation, films of any desired thickness can be built up [11].

When the thickness of the adsorbed film is over 500 nm and thus approaches the order of magnitude of the wavelength of visible light, the film becomes visible in reflected light, provided the refractive index of the film is between those of air and of the substrate. At a given angle of reflected light it exhibits an interference of colors. The average refractive index of the dry porous film of colloidal particles is usually less than that of glass [11].


Design of the Experiment

*Factorial design*

Some of the factors affecting the quality of our thin film coatings include the pH of the solution, the molarity of the solution, the uniformity of the nanoparticles, the centrifugal speed of the colloidal titania solution and the wash time of the slides. Therefore, it is of utmost importance that we are able to investigate many of these factors efficiently. If there are only two factors to be investigated, their effects on the thin film coatings can be easily deduced by holding one factor constant while varying the other factor. This is referred to as the “one-factor-at-a-time” (OFAT) method. In a study like ours, where many factors need to be investigated, OFAT is inefficient. Additionally, some factors may not have a large effect on their own, but may have a significant effect together with another factor. This is known as the interaction effect of two or more factors. By contrast to OFAT, in our experiments we use *factorial design*, an important statistical tool that allows us to investigate many factors at the same time and to also see responses of combinations of factors [13]. Factorial design has some other advantages such as needing fewer runs to have the same statistical power when compared to the OFAT
Suitable Substrates for Deposition

In our experiments, we use transparent microscope glass slides for the deposition of the nanoparticles. They are used because they are easy to obtain and are fairly inexpensive. Also it is quite easy to get rid of contamination from their surfaces which otherwise would affect transmittance and reflectance. Most importantly, upon cleaning, the glass slides acquire a negatively charged surface which provides a foundation for the deposition of our polycation (positively charged PDDA/PDA) solution. At this point the glass slides and polycation solution are oppositely charged, they adhere to each other. This provides the basis for the deposition of nanoparticles and the subsequent built up of multi-bilayers using LBL.

Preliminary cleaning

Firstly, the glass slides are cleaned thoroughly with acetone, with a piece of cloth which does not leave marks or scratch them. Secondly, the slides are cleaned with a procedure known as RCA cleaning which is described in the following section.

RCA procedure

Base Solution

(i).  5-1-1 to 7-2-1 (Water-Hydrogen peroxide-Ammonium hydroxide). Multiples of the base solution can be prepared depending on the amount that is desired to be used during the cleaning process.

(ii).  Stir the solution for a minute.

(iii).  Put the glass slides into the base solution contained in a glass staining jar.

(iv).  After mixing, put a cover on glass staining jars.

(v).  Place the glass jars in a Petri dish filled with preheated water ready to resume the desired temperature of 80 degrees.

(vi).  Heat the mixed basic solution containing the slides in the petri dish around 80 degrees C (+/- 5 degrees) for 20 minutes.
(vii). After 20 minutes, remove the glass slides very carefully, rinse each slide in DI water, and leave them in the glass jars containing DI water until they are ready to be placed in the acidic solution.

Acid Solution

(i). 6-1-1 to 8-2-1 (Water-Hydrogen peroxide-Hydrogen chloride). Again multiples of this ratio of the acidic solution can be prepared as desired.

(ii). Stir the solution for a minute.

(iii). Remove the glass slides from the glass jars containing the DI water and place the slides into the acidic solution contained in a glass staining jar.

(iv). After mixing, put a cover on glass jars.

(v). Wait for 20 minutes at room temperature.

(vi). After 20 minutes, rinse each slide with DI water.

(vii). Dry the slides with nitrogen gas and store it safely before the deposition of the colloidal silica and/or titania nanoparticles is done.

Werner Kern developed the basic procedure in 1965 while working for RCA, the Radio Corporation of America [14]. The purpose of the RCA clean is to remove organic contaminants (such as dust particles, grease or silica gel) from the glass surface; then remove any oxide layer that may have built up and finally remove any ionic or heavy metal contaminants [15]. The RCA clean procedure is usually performed immediately prior to any crucial step such as the deposition of the nanoparticles. For safety purposes these steps are carried out in a clean location such as a fume hood which is easily accessible in a science laboratory.

Preparing the nanoparticle colloidal suspension

First, the volume of suspension that will be required for the particular experiment is estimated in order to avoid any unnecessary wastage. The desired molarity of the suspension is then achieved by using the relation $C_{\text{initial}} V_{\text{initial}} = C_{\text{final}} V_{\text{final}}$

(i). $C_{\text{initial}}$ is the concentration of the bulk reserve nanoparticle suspension as purchased from the manufacturer.

(ii). $V_{\text{initial}}$ is the volume that is needed to be extracted carefully from the bulk reserve.
(iii). $C_{\text{final}}$ is the concentration of the nanoparticle suspension for the particular experiment.
(iv). $V_{\text{final}}$ is the estimated volume for the particular experiment.

$$V_{\text{initial}} = \frac{c_{\text{final}}V_{\text{final}}}{c_{\text{initial}}}.$$ Units are millimolar (milli moles per liter).

Since $C_{\text{initial}}$ usually has a very high value, only a small volume $V_{\text{initial}}$ is required. This volume is withdrawn using a 25ml pipette and transferred carefully to a graduated cylinder. De-ionized water is then used to bring this volume up to $V_{\text{final}}$. This process is repeated for three different molarities; for example, for Experiment 1, 350 mM, 1925 mM, and 3500 mM was prepared.

**Adjusting the pH of the nanoparticle colloidal suspension and the polycation solution**

After the suspension with a given molarity is ready, it has to be adjusted for the necessary pH. For Experiment 1, three different pH values of 7.5, 8.0 and 8.5 were used. This means that each of the three molarities is adjusted for three different pH values. Moreover, the PDDA solution is also adjusted for the same three pH values such that the nanoparticle suspension and the PDDA solution have the same pH for the deposition process.

pH adjustment is achieved by the addition of minute volumes of very dilute concentration of hydrochloric acid and/or sodium hydroxide (base) while the pH is being monitored by a pH meter. Once the pH is brought up to the required level, the process is ceased. The nanoparticle suspension and the polycation solution are now ready with the correct molarity and pH and available for deposition to take place.

**Layer-by-layer deposition**

The technique has been described earlier in the “Layer-by-layer self assembly of nanoparticles” section. The exact steps are as follows:

Two vials are prepared, one containing the PDDA solution and the other the silica/titania solution:

(i). The RCA cleaned slide is dipped into PDDA solution for 3 minutes. PDDA is a positively charged solution which adheres easily to the surface of the glass substrate as
after the RCA cleaning the glass substrate acquires a negatively charged surface. This is true for both the sides of the glass substrates.

(ii). The slide is extracted from the vial after 3 minutes and inserted the slide into a slide holder using tweezers.

(iii). Once the slide is inserted snugly, then it (slide with the slide holder) is placed in a petri dish filled with de-ionized water with a stirrer. The swirling of the water by the stirrer washes the excess reagents from the glass slides. This is done for 5 minutes.

(iv). After the washing, the slide is extracted from the slide holder and placed into the second vial containing the nanoparticle suspension for 3 minutes.

(v). After 3 minutes, the slide is washed again for 5 minutes and then placed into the PDDA solution again.

(vi). This cycle is continued until the desired number of bilayers is reached.

For example, PDDA(3 minutes) → Washing (5 minutes) → Silica (3 minutes) → Washing (5 minutes) → PDDA (3 minutes) ... washing (5 minutes) → drying with nitrogen gas → storing it safely.

**Drying**

Once the coating had been deposited on the glass slide, the glass slide is dried with flowing nitrogen gas and placed carefully in a container to avoid any scratches on the surface or contamination.

**Measuring the reflectance and the transmittance of the samples**

After the glass substrates with the deposited nanoparticles have dried out, it is time to measure their transmittance and reflectance. This is done using a Filmetrics F20-UV thin-film analyzer. We take a total of eight readings, four on each side of the treated glass slides. The measured values are averaged, and their standard deviation is used as a measure of the uniformity of the coatings.
We only analyze data in the interval of 380 nm – 750 nm, which is approximately the range of the visible spectrum. Transmittance and reflectance values vary with the wavelength, so we calculate an average value over the visible spectrum, which is then taken as the response in our analysis of the quality of the thin-film coatings.

**Challenges**

One of the biggest challenges in our experiment is that the thin films deposited on the glass slides are very unstable and fragile, so we have to exercise extreme caution when handling them. Also during the measurement of transmittance and reflectance, the films are disturbed upon being placed on the metal stage of the “thin-film analyzer”. Therefore, if the treated slides are to be kept for future reference, proper handling is required to keep the films intact.

Other minor challenges include the handling of concentrated hydrochloric acid and base for the RCA cleaning process. However, this has been easily overcome by using the proper gear consisting of a lab coat, thick goggles and gloves and proper shoes in the lab.

Another challenge is setting the pH of the nanoparticles suspension and the polycation suspension. However, after several hours of practice, the correct level of pH is easily reached.
Experiment One

Design

Experiment one was designed to investigate the following factors:

1. The pH of the nanoparticles suspension (values 7.5, 8.0 and 8.5).
2. The molarity of the nanoparticles suspension (values 350 mM, 1925 mM and 3500 mM).
3. The centrifugal speed of the titania suspension (labeled as RPM in our design; values 4000 rpm, 8000 rpm, and 12000 rpm). We know that titania nanoparticles are bigger than the silica nanoparticles and they tend to cluster. These clusters, if deposited on the microscope slides, would increase scattering of light. Therefore, we centrifuge the colloidal suspension prior to the deposition process and use centrifugal speed as one of our factors to determine to what extent these clusters affect with transmittance and reflectance.
4. The wash time (values 1 min, 3 min, and 5 min). The slides are washed with de-ionized water between dippings in the nanoparticle and polycation solutions and we use the wash time as one of the factors to see if its effect on the quality of the coatings is significant.

Once the factors to be investigated have been determined, they are input in a statistical software (Design-Expert 8) and the table shown below is obtained. This table contains detailed information on how the experiment would be carried out. After carrying out the experiment, the responses are measured and introduced in the table under the “responses” column. Each response is then analyzed to see what factor or combination of factors is statistically significant.
Figure 14. The complete design for Experiment One
Discussion

The complete half-normal plot for the effects on the transmittance

At a glance, the half-normal plot indicates that effects C, AB and B might be statistically significant. However, we use analysis of variance to double check.

ANOVA for transmittance

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<td>AD</td>
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Interaction effect of pH and molarity on transmittance

When the molarity is low, the line angles upward which indicates a positive effect on transmittance with increasing pH whereas when the molarity is high, the line angles downwards which indicates a negative effect on transmittance with increasing pH. Therefore, to maximize transmittance, with high pH, you have to use a low molarity and with low pH, use a high molarity.

Figure 16. Effect of the AB interaction on transmittance
Main effect of centrifugal speed on transmittance

From Figure 17, we can see that an increase in transmittance is achieved with a greater centrifugal speed of the titania suspension.
Main effect of molarity on transmittance

From Figure 18, transmittance is notably increased when a low molarity is used. However, as discussed above, molarity is involved in an interaction. As such, from the interaction of pH and molarity, a high pH would have to be used when using low molarity to achieve increased transmittance.
The complete half-normal plot for the effects on the reflectance

Figure 19. Model for reflectance

From Figure 19, it is quite clear that B is statistically significant whereas C, D, AC and AD are very close to the line emanating from the origin which may be the result of normal scatter.

ANOVA for reflectance

<table>
<thead>
<tr>
<th>Factor</th>
<th>P value</th>
<th>Significant/ Insignificant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.0009</td>
<td>Significant</td>
</tr>
<tr>
<td>B- Molarity</td>
<td>0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>C-RPM</td>
<td>0.1053</td>
<td>Insignificant</td>
</tr>
<tr>
<td>D-Wash time</td>
<td>0.1494</td>
<td>Insignificant</td>
</tr>
<tr>
<td>AC</td>
<td>0.0925</td>
<td>Maybe significant</td>
</tr>
<tr>
<td>AD</td>
<td>0.1140</td>
<td>Insignificant</td>
</tr>
</tbody>
</table>
Interaction effect of pH and centrifugal speed on reflectance

From Figure 20, when the centrifugal speed is low, the line is sloping downwards with increasing pH. This indicates a negative effect but one which is desirable as the goal is to reduce reflectance. However, when the centrifugal speed is high, reflectance is increased with increasing pH which is not desirable. Therefore, to reduce the reflectance, a lower centrifugal speed with a higher pH should be used. On the other hand low reflectance is achieved when higher centrifugal speed with a lower pH is used. An important thing to note is that the least significant difference bars are overlapping significantly for both the low and high centrifugal time and the two lines are reclining or declining only marginally. This means that the reflectance is almost unaffected by low or high centrifugal speed with increasing pH. This is supported by the p-value for AC which is 0.0925.
Main effect of molarity on reflectance

From Figure 21, a low molarity is needed to reduce reflectance. This is consistent with our discussion above whereby a low molarity was needed to increase transmittance.
The complete half-normal plot for the effects on the extinction

From Figure 22, effects B, AB, AD, D and C are likely significant.

ANOVA for extinction

<table>
<thead>
<tr>
<th>Factor</th>
<th>P value</th>
<th>Significant/ Insignificant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.0159</td>
<td>Significant</td>
</tr>
<tr>
<td>B- Molarity</td>
<td>0.1014</td>
<td>Insignificant</td>
</tr>
<tr>
<td>C-RPM</td>
<td>0.0255</td>
<td>Significant</td>
</tr>
<tr>
<td>D-Wash time</td>
<td>0.0600</td>
<td>Significant</td>
</tr>
<tr>
<td>AB</td>
<td>0.0950</td>
<td>Maybe significant</td>
</tr>
<tr>
<td>AD</td>
<td>0.0834</td>
<td>Maybe significant</td>
</tr>
</tbody>
</table>
Interaction effect of pH and molarity on extinction

From Figure 23, when the molarity is low, the line slopes downward with increasing pH. This is desirable as this leads to reduced extinction. On the other hand when the molarity is high, the line slopes upward with increasing pH. This condition is not favorable. That is, for a low extinction, a low molarity and a high pH is needed or a high molarity and a low pH is required. This correlates well with our discussion above as these were the same conditions that were needed to increase transmittance.
Interaction effect of pH and wash time on extinction

Figure 24. Effect of the AD interaction on extinction

From Figure 24, when the wash time is low, the extinction increases with increasing pH and when the washing time is high, the extinction decreases with increasing pH. Therefore, in order to have a low extinction a high pH and a high wash time is required and vice versa. However, as indicated by the ANOVA, this interaction might only be remotely significant as also shown by the overlap of the LSD bars.
Main effect of centrifugal speed on extinction

From Figure 25, a high centrifugal speed leads to reduced extinction.
Main effect of wash time on extinction

From Figure 26, a high wash time leads to reduced extinction.
The complete half-normal plot for the effects on the relative standard deviation of transmittance

The half-normal plot in Figure 27 indicates that the interaction effect AD is significant whereas the effects A, B, C, AB and AC are maybe significant.

ANOVA for relative standard deviation for transmittance

<table>
<thead>
<tr>
<th>Factor</th>
<th>P value</th>
<th>Significant/ Insignificant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.0077</td>
<td>Significant</td>
</tr>
<tr>
<td>A-pH</td>
<td>0.0777</td>
<td>Significant</td>
</tr>
<tr>
<td>B- Molarity</td>
<td>0.1154</td>
<td>Insignificant</td>
</tr>
<tr>
<td>C-RPM</td>
<td>0.1872</td>
<td>Insignificant</td>
</tr>
<tr>
<td>AB</td>
<td>0.2392</td>
<td>Insignificant</td>
</tr>
<tr>
<td>AC</td>
<td>0.0836</td>
<td>Maybe significant</td>
</tr>
<tr>
<td>AD</td>
<td>0.0018</td>
<td>Significant</td>
</tr>
</tbody>
</table>
Interaction effect of pH and centrifugal speed on relative standard deviation of transmittance

From Figure 28, when centrifugal speed is at the low level, the line is almost horizontal which means that relative standard deviation for transmittance is almost unaffected with increasing pH. On the other hand, when the centrifugal speed is high, the line slopes downwards which means that the relative standard deviation decreases with increasing pH. Therefore, to reduced relative standard deviation for transmittance, a high pH is required.
Interaction effect of pH and wash time on relative standard deviation of transmittance

Figure 29. Effect of the AD interaction on the relative standard deviation for transmittance

From Figure 29, when wash time is low, the relative standard deviation increases with increasing pH which is shown by the line sloping upwards. On the other hand, when the wash time is high, the line slopes downwards which indicates that the relative standard deviation decreases with increasing pH. Therefore, to have a low standard deviation, high wash time and high pH should be used or a low wash time and low pH should be used.
Main effect of pH on the relative standard deviation of transmittance

From Figure 30, a low pH gives a reduced standard deviation for transmittance which is desirable.
The complete half-normal plot for the effects on the relative standard deviation of reflectance

The half-normal plot indicates that B and AC are not significant as they form part of the normal scatter, that is, they fall on the line emanating from the origin.

**ANOVA for relative standard deviation for transmittance**

<table>
<thead>
<tr>
<th>Factor</th>
<th>P value</th>
<th>Significant/ Insignificant</th>
</tr>
</thead>
<tbody>
<tr>
<td>model</td>
<td>0.2745</td>
<td>Insignificant</td>
</tr>
</tbody>
</table>

Using ANOVA, the model is deduced to be statistically insignificant; therefore, no further analysis will be carried out for this model.
The complete half-normal plot for the effects on the Rayleigh slope

From a glance at the half normal plot for the Rayleigh slope, effects B, D and AC might be statistically significant.

ANOVA for Rayleigh slope

<table>
<thead>
<tr>
<th>Factor</th>
<th>P value</th>
<th>Significant/ Insignificant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.0026</td>
<td>Significant</td>
</tr>
<tr>
<td>B- Molarity</td>
<td>0.0103</td>
<td>Significant</td>
</tr>
<tr>
<td>D-Wash time</td>
<td>0.0098</td>
<td>Significant</td>
</tr>
<tr>
<td>AC</td>
<td>0.0501</td>
<td>Significant</td>
</tr>
</tbody>
</table>
Interaction effect of pH and centrifugal speed on the Rayleigh slope

From Figure 33, when the centrifugal speed is low, the line slopes upwards with increasing pH. This is not desirable. We would like to have a low Rayleigh slope as this will indicate that there is less scattering. On the other hand when the centrifugal speed is high, the line slopes downwards with increasing pH. This is favorable as it indicates less scattering from the treated glass substrates. Therefore, to have a low Rayleigh slope, a low centrifugal speed and low pH is needed or a high centrifugal speed and a high pH is needed.
Main effect of molarity on the Rayleigh slope

From Figure 34, it can be seen that a low molarity is required to have a low Rayleigh slope.
Main effect of wash time on Rayleigh slope

From Figure 35, it can be seen that a high wash time is needed to have low the Rayleigh slope.
Summary

The table below summarizes the analysis done in the previous section.

| Maximizing Transmittance | • Use low molarity and high pH.  
|                          | • Use high molarity and low pH.  
|                          | • Use high centrifugal speed  
|                          | • Use low molarity  
| Minimizing Reflectance   | • Use low molarity  
| Minimizing Extinction    | • Low molarity and high pH  
|                          | • High molarity and low pH  
|                          | • Low wash time and smaller pH.  
|                          | • High wash time and high pH  
|                          | • High centrifugal speed  
|                          | • High wash time  
| Minimizing relative standard deviation for transmittance | • High centrifugal speed and high pH  
|                          | • High wash time and high pH  
|                          | • Low wash time and low pH  
| Minimizing relative standard deviation for reflectance | • Insignificant model  
| Minimizing the Rayleigh slope | • High RPM and high pH  
|                          | • Low RPM and low pH  
|                          | • Low molarity  
|                          | • High wash time  

For Experiment 1, it was determined that the factors which gave optimum results were a low molarity of the nanoparticles solution, a high pH, a high centrifugal speed for the titania suspension and a high wash time.
Experiment Two.

Design

Experiment 2 was designed taking into consideration the results from Experiment 1. There were only two factors that were investigated:

1. Number of titania bilayers
2. Number of silica bilayers

The other factors investigated in Experiment 1 were used at the levels that were found to give optimum results, that is, low molarity, high pH, high centrifugal speed for the titania suspension and high wash time.

The purpose of this design was to introduce the basic unit of a periodic system called “double-quarter”, whereby an alternating high- and low-index material is used to compose the thin films on the glass slides. Experiment 2 only deals with a single layer, that is, \( n_H/n_L \) whereby the stack of silica bilayers provide the high index material and the stack of titania bilayers provide the low index material as show in the figure below;

![Diagram](image)

Figure 36. Double-quarter structure [8]

The aim of this arrangement is to increase the range of wavelengths for which low reflectance and high transmittance are achieved [8].
Discussion

The table below shows all the factor-level combination used, as well as the six responses that were taken into account in the analysis: transmittance, reflectance, extinction, Rayleigh slope, relative standard deviation for transmittance, and relative standard deviation for reflectance.

![Table showing factor levels and responses](image)

Figure 37. The complete design for Experiment 2.
The complete half-normal plot for the effect on the transmittance

From the half normal plot in Figure 38, effect B, which is the number of layers of silica nanoparticles, seems to be statistically significant.

ANOVA for transmittance

<table>
<thead>
<tr>
<th>Factor</th>
<th>P value</th>
<th>Significant/ Insignificant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.0003</td>
<td>Significant</td>
</tr>
<tr>
<td>B- Silica</td>
<td>0.0003</td>
<td>Significant</td>
</tr>
</tbody>
</table>
Main effect of silica bilayers on transmittance

From Figure 39, to achieve a high transmittance, a low number of silica nanoparticles layers is desirable.
The complete half-normal plot for the effects on the reflectance

![Half-Normal Plot](image)

**Figure 40. Model for the reflectance**

Again from the half normal plot in Figure 40, Effect B, which is the number of layers of silica nanoparticles, seem to be statistically significant.

**ANOVA for reflectance**

<table>
<thead>
<tr>
<th>Factor</th>
<th>P value</th>
<th>Significant/ Insignificant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>&lt;0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>A-Titania</td>
<td>0.1271</td>
<td>Insignificant</td>
</tr>
<tr>
<td>B- Silica</td>
<td>&lt;0.0001</td>
<td>Significant</td>
</tr>
</tbody>
</table>
Main effect of silica bilayers on reflectance

From Figure 41, to minimize reflectance, a lower number of silica nanoparticles layers is needed. This is consistent with our discussion above in which to maximize transmittance a lower of silica layers was needed.
The complete half-normal plot for the effects on the extinction

From Figure 42, it is possible that effect B has statistical significance.

ANOVA for extinction

<table>
<thead>
<tr>
<th>Factor</th>
<th>P value</th>
<th>Significant/ Insignificant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.0237</td>
<td>Significant</td>
</tr>
<tr>
<td>B- Molarity</td>
<td>0.0237</td>
<td>Significant</td>
</tr>
</tbody>
</table>
Main effect of silica bilayers on extinction

<table>
<thead>
<tr>
<th>Design-Expert® Software</th>
<th>Extinction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design Points</td>
<td></td>
</tr>
<tr>
<td>X1 = B: Silica</td>
<td></td>
</tr>
</tbody>
</table>

Actual Factor
A: Titania = 4

From Figure 43, a lower number of silica nanoparticles layers are desired to reduce extinction. This is also consistent with our discussion from above whereby a lower number of silica nanoparticles layers were needed to have a high transmittances and low reflectance.
The complete half-normal plot for the effect on the relative standard deviation for transmittance

From the half normal plot in Figure 44, none of the Effects A, B and AB are significant as they form part of the normal scatter.

**ANOVA for relative standard deviation for transmittance**

<table>
<thead>
<tr>
<th>Factor</th>
<th>P value</th>
<th>Significant/ Insignificant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.4329</td>
<td>Insignificant</td>
</tr>
</tbody>
</table>

Since the model is declared insignificant, no further analysis will be carried out for it.
The complete half-normal plot for the effect on the relative standard deviation of reflectance

From Figure 45, effect B, which is the number of silica layers, is significant.

ANOVA for relative standard deviation for reflectance

<table>
<thead>
<tr>
<th>Factor</th>
<th>P value</th>
<th>Significant/ Insignificant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.0029</td>
<td>Significant</td>
</tr>
<tr>
<td>B- Molarity</td>
<td>0.0029</td>
<td>Significant</td>
</tr>
</tbody>
</table>
Main effect of silica bilayers on relative standard deviation of reflectance

From Figure 46, to reduce the relative standard deviation, 6 layers are preferred. This observation deviates slightly from our discussion above in which a lower number of silica layers were preferred.
The complete half-normal plot for the effect on the Rayleigh slope

From Figure 47, once again it seems that effect B, which is the number of silica layers is statistically significant.

ANOVA for Rayleigh slope

<table>
<thead>
<tr>
<th>Factor</th>
<th>P value</th>
<th>Significant/ Insignificant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.0056</td>
<td>Significant</td>
</tr>
<tr>
<td>B- Molarity</td>
<td>0.0056</td>
<td>Significant</td>
</tr>
</tbody>
</table>
Main effect of silica bilayers on Rayleigh slope

From Figure 48, it can be seen that to have a low Rayleigh slope, which indicates less scattering, a lower number of silica nanoparticles layers is desired.
Summary

| Maximizing Transmittance                      | Low number of silica bilayers |
| Minimizing Reflectance                        | Low number of silica bilayers |
| Minimizing Extinction                         | Low number of silica bilayers |
| Minimizing relative standard deviation for transmittance | • Insignificant model |
| Minimizing relative standard for reflectance  | A higher number of silica bilayers |
| Minimizing the Rayleigh slope                 | • Low number of silica bilayers |

From Experiment 2, it was determined that the factor-level combination which gave the optimum result was a low number of silica bilayers whereas the number of titania bilayers were statistically insignificant. This means that for the basic periodic structure, a low number of silica bilayers is sufficient to provide the suitable high index material.
Conclusion and Future Directions

The major goal of this research project was to demonstrate an effective and inexpensive method of producing antireflective coatings using layer-by-layer self-assembly of nanoparticles. The statistical analysis of the responses allowed us to determine the experimental factors that have a significant effect on transmittance, reflectance and extinction.

The results from experiment one suggest that in order to maximize transmittance and minimize reflectance we should use a low molarity silica solutions with high pH, centrifuge the titania at a high speed and increase the wash time of the slides. The results from experiment two suggest that higher transmittance, lower reflectance and less extinction are achieved with a smaller number of nanoparticles bilayers.

Some of the factor-level combinations yielded coatings with transmittances in excess of 96%, well above the value for an untreated glass substrate, and comparable with commercial coatings. However, the results from experiment two were not completely satisfying as we were not able to reach a definitive conclusion on the number of titania bilayers we should use for future experiments. In experiment two, the double-quarter structure was introduced as a basic unit for the quarter-wave stack structure which we intend to use in future experiments.

One aspect to be considered in future research is that the coatings are not robust and get scratched very easily. If these thin films are intended for camera lenses or other such applications, their mechanical qualities should be improved. The films would have to be more stable and durable and be able to withstand the elements.

Overall, this research project had satisfactory results which lay a solid foundation in the study of self-assembled antireflective coatings made of silica and titania nanoparticles.
References


Appendix

Design using “Design –Expert”

Once the number of factors and responses for a particular experiment has been determined, it is time to design the experiment using the “Design – Expert” (software for design of the experiments).

1. To build the design, choose File, New.

2. Then from the default **Factorial** tab, click **2-level factorial**. From the horizontal axis, select the number of factors that is to be investigated and from the vertical axis select the number of runs that is desired. More runs will always equal more information. If you are looking at those designs that has only 4 or 8 runs you have to be careful as it cannot estimate the AB interaction if you do not replicate. The 4 and 8 runs designs have very low power. This means that your effects must be very large relative to the noise in your process in order for this design to be able to detect those effects. In this page, other information such as “Replicates”, “Blocks” and “Center points per block “can also be filled.

   a. Replicates - generally, it does not make sense to replicate fractional factorial designs. Rather than replicate, choose a higher resolution design and then you will obtain more information as well as gain power. If you are taking repeated sample or measuring the responses several times for a given run, that raw data should be entered into a spreadsheet. From the spreadsheet calculate the average and standard deviation of the raw data and then enter that information as two responses into Design-Expert.

   b. Blocking is done to restrict the randomization in order to use a resource that is not being studied. For example, if you need to use 2 different samples of PDPA solution
prepared separately (with the same pH, molarity etc) or the experiment will take place
over 3 days. The variation due to the difference between the materials, or the
difference between the days, is removed from the analysis before the factor effects are
calculated.

c. Centerpoints are implemented to validate that the factor effect relationships are linear.
4 – 5 centerpoints are recommended. Refer to the illustration below

From the illustration above, for Experiment 1, it was determined that four factors will be
investigated for 8 runs. It was also decided that the there would be two replicates, two blocks and
4 center points.
3. Click the **Continue** button and enter all the required information for the factors, units, type, the low values and the high values.

4. Click **Continue** to go the next page which requests for the name of the blocks. Not necessary as it could just be left as 1 and 2.
5. **Continue** again to the next page which requests information for the number of responses.
6. The next step takes you to the complete design shown below. At this point in time you have all the required information to proceed to the experimental part of the research. The illustration below shows the various combinations of factors that would be investigated. For example, for run 1, the titania nanoparticle colloidal suspension should have a concentration of 3500 mM and its pH would be adjusted to approximately 7.5. This solution would be centrifuged at 4000 rev/min and the slides that would be dipped in this suspension would be washed for 5 minutes upon removal. Also note that the last 6 columns are empty. These columns would be utilized once the experiment has been completed and the responses have been calculated. The calculated responses would then be copied and pasted into these empty columns for the analysis of the data.