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Polymer Mediated Layer-by-layer Assembly of Different Shaped Gold Nanoparticles

Stephen M. Budy^a, Desmond J. Hamilton^a, Yuheng Cai^b, Michelle K. Knowles^b, and Scott M. Reed^a

^aDepartment of Chemistry, University of Colorado Denver, Denver, CO, USA 80204

^bDepartment of Chemistry and Biochemistry, University of Denver, Denver, CO, USA 80208

Abstract

Gold nanoparticles (GNPs) have a wide range of properties with potential applications in electronics, optics, catalysis, and sensing. In order to demonstrate that dense, stable, and portable samples could be created for these applications, multiple layers of GNPs were assembled via drop casting on glass substrates by layer-by-layer (LBL) techniques. Two cationic polyelectrolytes, poly(diallyldimethylammonium chloride) and polyethyleneimine, one anionic polyelectrolyte, poly(sodium 4-styrene sulfonate), and one neutral polymer, polyvinylpyrrolidone, were combined with four different shapes of GNPs (spherical, rod, triangular prismatic, and octahedral) to prepare thin films. A subset of these polymer nanoparticle combinations were assembled into thin films. Synthesized GNPs were characterized via dynamic light scattering, UV-vis spectroscopy, and transmission electron microscopy and the LBL thin films were characterized using UV-vis spectroscopy and atomic force microscopy. Sensing applications of the nanoparticles in solution and thin films were tested by monitoring the localized surface plasmon resonance of the GNPs. LBL thin films were prepared ranging from 25 to 100 layers with optical densities at plasmon from 0.5 to 3.0. Sensitivity in solutions ranged from 14 to 1002 nm/RIU and films ranged from 18.8 to 135.1 nm/RIU suggesting reduced access to the GNPs within the films.

Graphical Abstract

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Correspondence to: Scott M. Reed.

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1. Introduction

Over the past decade there has been increasing evidence for the utility of the localized surface plasmon resonance of metal nanoparticles.^{1–3} Applications have been found in nonlinear optics,⁴ optical recording,⁵ biolabeling,⁶ biosensors,^{7–9} and phototherapy.¹⁰ In some cases the immobilization of metal nanoparticles on a transparent solid-state substrate would provide for new opportunities. Therefore, the development of efficient techniques for making thin films with tailored and controlled parameters from a variety of metal nanoparticles is critical for the realization of practical devices. The size, shape, and charge of a nanoparticle alters its intrinsic optical properties but also effects how that nanoparticle assembles to varying densities in the presence of a dielectric coating.¹¹ The synthesis and control over particle shape and size has been significantly improved in the past few years with shapes including spheres,^{12, 13} rods,^{14–16} platelets,^{17, 18} cages,¹⁹ polyhedrons,²⁰ and stars²¹ now demonstrated. A number of studies have looked at the optical effects caused by changes in the refractive index (RI), including our recent study using the localized surface plasmon resonance of GNPs to monitor lipid membrane assembly and protein binding.²²

Layer-by-layer (LBL) assembly is a versatile and inexpensive approach to solid-state thin film formation.^{23, 24} Researchers have been interested in the production of thin films using LBL assembly for coatings and smart surfaces at the molecular level for many applications.²⁵ The advantages of the LBL assembly technique are simplicity and control of thickness at the nanoscale level. The LBL technique allows for the introduction of many components with high loadings in the assembled layers, and each layer can be optimized for specific applications.²⁶ The thickness of each layer and the properties of the film depend upon the chemistry used to connect the layers (*i.e.*, charge density, pH, molecular weight, temperature, deposition time, and concentration).²⁷ LBL was originally developed for polyelectrolyte/polyelectrolyte systems, but now the ability of LBL to control the thickness, properties, and economics make the assembly tool ideal for creating nanoparticle films.²⁸

A handful of studies have examined how interactions between the metal nanoparticles within a film effect the plasmon and the nanoparticle density within the films.^{29–31} Early work showed that simple organic linkers between layers resulted in substantial red-shifting over the course of depositing eight layers. Building off of early work with semiconductor nanoparticles,²³ Ung *et al.* showed that sixteen layers of silica-encapsulated GNPs could be assembled using polyelectrolyte LBL assembly.³² When GNPs were coated instead with a small cationic ligand and assembled by LBL there was a surprising 13 nm blue-shift during the deposition of subsequent layers.^{27, 33} The amount of red-shift for the particles could be tuned from a few nm to over 100 nm by changing the thickness of the silica coating on the gold. With less of a coating, there is a stronger red-shift and broadening of the plasmon band of the particles as the interparticle distance is reduced. While the efficiency of solid-state devices will increase with higher particle density it is also important to maintain access of analytes to the nanoparticle surface for sensing applications.

Few reports have examined LBL assembly of asymmetric nanoparticles.³⁴ When nanorod assembly by LBL was explored³⁵ a substantial red-shift was observed after only 4 layers of nanorod deposition. Thin films of spin assisted LBL cross-linked hydrogels were swollen

and soaked in gold nanorods.³⁶ Minimal red-shifting and broadening was observed, however the absorbance never exceeded 0.5 which indicated low loadings of GNPs. And because the LBL film was prepared and cross-linked before the GNP loadings it is likely the diffusion of GNPs would be limited to the surface and outer edges. Thin films were assembled by electrostatic LBL using GNPs and bovine serum albumin-functionalized graphene sheets for electrochemical sensing.³⁷ After only 5 layers, red-shifting and broadening occurred and after 10 layers the absorbance was less than 0.4. It remains a challenge to precisely control plasmonic coupling and access of analytes in these films while achieving a high nanoparticle density.

The purpose of this work was to optimize methods of forming dense nanoparticle thin films using a variety of GNP shapes using four different polymers that permit analyte access to the nanoparticles on the film surface. To the best of our knowledge, this is the first report using a drop casting LBL method to prepare highly packed GNP films. High particle density (maximum optical density between 0.5 and 3.0) was achieved in each optimized case without coating the particles beforehand. The optical effects resulting from the growth of each layer were followed up to 100 layers of deposition by measuring the LSPR. Lastly, access to the surface was assessed by measuring the sensitivity of the localized surface plasmon resonance of each GNP shape in a layer-by-layer thin film and comparing it to the response of the same nanoparticles in solution.

2. Experimental

Materials

L- α -Phosphatidylcholine (Type IV-S, 30% from soybean, PC₃₀), polyvinylpyrrolidone (average molecular weight 10,000 g/mol, PVP), polyethyleneimine (average molecular weight 50,000 g/mol, 50 wt% in H₂O, PEI), poly(sodium 4-styrene sulfonate) (average molecular weight 100,000 g/mol, PSS), poly(diallyldimethylammonium chloride) (average molecular weight 400,000 g/mol, 20 wt% in H₂O, pDADMAC), sodium borohydride (0.5 M in 2-methoxyethyl ether, NaBH₄), and ethylene glycol (anhydrous, 99.8%) were from Sigma-Aldrich. L-(+) ascorbic acid was from MCB, silver nitrate was from EM Science, sodium borohydride was from Acros, cetyltrimethyl ammonium bromide (CTAB) was from B-Biosciences, and hydrogen tetrachloroaurate(III) hydrate (99.9% Au, HAuCl₄ xH₂O) and hydrogen tetrabromoaurate(III) hydrate (99.9% Au, HAuBr₄ xH₂O) were from Strem Chemicals and all were used without further purification unless otherwise mentioned. All water was from a Milli-Q Integral Water Purification System from EMD Millipore and had a resistance of 18.1 M Ω cm. Glass microscope slides were obtained from Corning (2947, 75 $\times$ 25 $\times$ 1 mm).

Instrumentation

Dynamic light scattering (DLS) measurements were recorded on a Zetasizer Nano S90 (Malvern Instruments, Worcestershire, United Kingdom). Mean hydrodynamic radius was obtained from the intensity distribution. UV-visible spectra were measured on a Perkin-Elmer Lambda 650 UV/Vis spectrometer (PerkinElmer, Waltham, Massachusetts) from 400 to 900 nm using a 1 nm slit width. Transmission electron microscopy (TEM) was performed

with a Philips EM 300 TEM (Philips Electron Optics, Eindhoven, The Netherlands) operating at 120 kV equipped with a charge-coupled device (CCD) camera. Samples were prepared by drop casting (5 μ L) aqueous solutions of nanoparticles onto Formvar films on copper grids (FCF300-Cu, Electron Microscopy Sciences). Samples were dried for 24 h before images were collected. AFM measurements were performed on a Dimension 3100 AFM (Digital Instruments) and obtained in tapping mode using a silicon nitride tip cantilever (OTESPA(A), Bruker). The cantilever oscillation frequency was set at 335 kHz. AFM images were analyzed using NanoScope Analysis (ver 1.50, Bruker). TEM images were analyzed using ImageJ image analysis software (ver 1.4.7, Wayne Rasband, NIH). LSPR measurements of GNPs were performed using a deuterium-tungsten halogen light source (DH-2000, Ocean Optics) and extinction spectra were collected with a fiber-coupled Ocean Optics HR4000. Integration times of 22 ms per spectrum and averaging of 50 spectra per data set were used to optimize the signal-to-noise ratio. Data analysis was performed using custom-built MATLAB script¹⁹ performed on spectra to extract three characteristic parameters describing the LSPR peak: the optical density (OD), the full width at half-maximum (FWHM), and the resonant wavelength (by calculating the centroid of the peak above the region marked by the FWHM). The value of the centroid has been shown to track linearly with the LSPR peak while providing an improved signal-to-noise ratio.³⁸

Gold nanoparticle (GNP) synthesis via citrate

Sodium citrate-capped spherical GNPs were prepared by a literature method.³⁹ Tetrachloroaurate(III) hydrate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$, 5 mg, 14.7 μ mol) was dissolved in 95 mL water (Milli-Q) and refluxed. A 1% sodium citrate solution ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, 34 mM) was prepared and 5 mL (170 μ mol) was added to the boiling solution. The solution was refluxed for 30 min and then left to cool to room temperature. The average diameter was 20 nm as characterized via DLS and TEM.

GNP synthesis via phosphatidylcholine

Phosphatidylcholine (PC)-coated spherical GNPs were prepared based on modifications to our literature method.⁴⁰ PC^{30} (200 mg, 80 μ mol) was dissolved in a minimal amount (1–2 mL) of cyclohexane. This solution was dried by rotary evaporation or under a stream of nitrogen followed by drying under vacuum to yield a thin film. The film was then re-suspended in Milli-Q water (20 mL) and sonicated for 30–60 min until the solid was fully suspended. DLS showed the average hydrodynamic diameter of the liposomes was less than 200 nm. In a clean scintillation vial, the gold bromide seed solution was freshly prepared for each experiment. HAuBr_4 (10 mM, 125 μ L) was added to a PC_{30} stock (2 mL) and H_2O (3 mL). NaBH_4 (10 mM, 300 μ L) was quickly added and the resulting purple seed solution was stirred for 30 min prior to use. In a clean scintillation vial, GNPs were synthesized by diluting PC_{30} stock (2 mL) with Milli-Q water (15 mL). To this stirred solution was added HAuBr_4 (10 mM, 400 μ L) and then gold seed (40 μ L). Freshly prepared ascorbic acid (100 mM, 40 μ L) was quickly added and the solution immediately became transparent and then darkened to a red color within 3–5 min. The resulting solution was stirred 18–20 h prior to use. The average diameter was 20 nm via DLS and TEM.

CTAB-coated rod-shaped GNPs

Modifications were made to a previous method.⁴¹ To prepare gold seed, tetrachloroaurate(III) hydrate (10 mM, 250 μ L) was added to CTAB (100 mM, 7.5 mL) in a 20 mL scintillation vial. The brown-yellow solution was mixed gently by inversion. Cold sodium borohydride (10 mM, 600 μ L) was added quickly, followed by mixing via rapid inversion for 30 s intervals for 2 min, and uncapping in between each interval to allow the escape of evolved gas. The seed solution was kept in a water bath at 25–30 °C for 3–5 h. Rod-shaped GNPs were prepared in a 20 mL scintillation vial. CTAB (100 mM, 9.5 mL), HAuCl₄ (10 mM, 400 μ L), and AgNO₃ (10 mM, 60 μ L) were added sequentially and the vial was capped and then gently mixed via inversion. Ascorbic acid (100 mM, 64 μ L) was added to the yellow solution which immediately became colorless. Finally, the seed solution (20 μ L) was added, and the reaction mixture was gently mixed via inversion for 10 s turning a purple color and then left undisturbed for 3–5 h. The GNPs were cleaned by centrifuging for 15 min at 15,000 $\times$ g to precipitate the solid. The colorless supernatant was discarded. The pellet was re-dispersed in Milli-Q water and sonicated for 15–20 min. Centrifugation was repeated twice. The average dimensions were 100 nm length and 15 nm width as characterized by TEM image analysis.

PC-coated triangular prismatic GNPs

Modifications were made to our previous method.⁴⁰ PC₃₀ (200 mg, 80 μ mol) was dissolved in a minimal amount (1–2 mL) of cyclohexane. A thin film was formed by rotary evaporation for 1 hour or a stream of nitrogen and then dried under vacuum. The film was then re-suspended in Milli-Q water (20 mL) and minimally vortexed until the solid was fully suspended and DLS showed a hydrodynamic diameter of approximately 300 nm. In a clean 20 mL scintillation vial the gold chloride seed solution was freshly prepared for each experiment. HAuBr₄ (10 mM, 125 μ L) was added to a PC₃₀ stock (2 mL) and H₂O (3 mL). NaBH₄ (0.5 M in 2-methoxyethyl ether, 6 μ L) was quickly added and the resulting purple seed solution was allowed to stir for 30 min prior to use. In a clean large Kimex® media bottle, GNPs were synthesized by diluting PC₃₀ stock (12 mL) with Milli-Q water (90 mL). To this stirred solution was added HAuBr₄ (10 mM, 2.4 mL) and then gold seed (200 μ L). Freshly prepared ascorbic acid (100 mM, 440 μ L) was quickly added and the solution immediately became transparent and then darkened to a purple color within 3–5 min. The resulting solution was allowed to stir for 24 h prior to use. Both spherical and triangular prismatic GNPs were present. The average diameter and edge length for the spherical particles and triangular prismatic particles was 20 and 90 nm, respectively, via DLS and TEM. In order to isolate the PC-coated triangular prismatic GNPs, a sucrose gradient was performed ranging from 40–80% sucrose in 50 mL Falcon® tube. Centrifugation using a swinging bucket rotor at 2000 $\times$ g for 2 h sufficiently separated the spheres into the 40–50% sucrose bands and triangular prisms into the 80% sucrose band. Collection of the separate fractions and centrifugation using a fixed rotor at 5000 $\times$ g for 10 min pelleted the GNPs. The colorless sucrose supernatant was discarded. The pellet was re-dispersed in Milli-Q water and sonicated for 15–20 min. Centrifugation was repeated three times. The average edge length was 90 nm as characterized by DLS and TEM.

pDADMAC-coated octahedral GNPs

Modifications were made to a previous method.⁴² Ethylene glycol (10 mL), pDADMAC (200 mg), and H₃PO₄ (1 M, 400 μ L) were added to a 20 mL scintillation vial and vortexed for 30 s. HAuCl₄ (0.5 M, 10 μ L) was added to the colorless solution and vortexed for an additional 60 s. The golden yellow solution was tightly capped and wrapped with electrical tape, and then the solution was loaded into a 195 °C oil bath for 30 min while stirring (*CAUTION: contents are HOT and under HIGH PRESSURE!*). During the reaction, the color of the solution changed from yellow to colorless and then, gradually, to purple and finally brown. The reaction was cooled to room temperature and centrifuged at 20,000 $\times$ g for 30 min and re-dispersed in Milli-Q water and sonicated for 30 min. This was repeated at least three times. The average hydrodynamic diameter was 50 nm as characterized by DLS and edge length by TEM.

Layer-by-layer (LBL) assembly

Microscope glass slides were cut to 1 $\times$ 3 cm using a diamond scribe. The substrates were cleaned by immersion in sodium hydroxide (5 M) for 60 min, followed by extensive rinsing with Milli-Q water, then immersion in freshly prepared aqua regia (3:1, HCl/HNO₃) (*CAUTION: aqua regia is a powerful oxidizing agent and strong acid!*) for 60 min, followed by rinsing with Milli-Q water, and finally drying in an oven for 30 min. All of the polymer solutions were prepared at 1 mg/mL in 0.5 M NaCl. Each polymer solution was filtered using a 0.1- μ m syringe filter (PTFE, Whatman) and drop cast (150 μ L) on separate glass substrates for 30 min, followed by rinsing with Milli-Q water, and dried under a nitrogen stream. GNPs were used as synthesized and not filtered, but vortexed for 10 s before each deposition. A layer of each GNP was deposited separately on each polymer by drop casting 125 μ L for 15 or 30 min, followed by rinsing with Milli-Q water. The sample was dried under a nitrogen stream after each deposition. Optical properties were measured after each deposition layer (consisting of one layer each of polymer and GNPs) for the first five layers and then subsequently every five layers. All measurements were recorded in the dry state except for LSPR experiments which were recorded in Milli-Q water.

3. Results and Discussion

3.1. Synthesis of gold nanoparticles

As more applications are being developed utilizing near infrared (NIR) active NPs, methods for assembling materials containing these NPs must be optimized. Therefore, different size and shape GNPs were synthesized according to methods developed in our laboratory and in the literature to study layer-by-layer sample preparations. Analysis by TEM (Figure 1) revealed the as-prepared particles were representative of the shape and size of the GNPs desired. Citrate-capped spheres were prepared from the Turkevich method³⁹ and had an average diameter of 20 nm (not shown). The PC-coated sphere (Figure 1A) and PC-coated prism (Figure 1C) method⁴⁰ was developed in our laboratory and lead to an average diameter of 20 nm and average edge length of 90 nm, respectively. We optimized the purification of large scale PC-coated prism synthesis using a simple, quick, and inexpensive sucrose density method via centrifugation for 2 h, which is much less than other reports taking 12 h using more expensive surfactants.⁴³ However, the purification does not lead to

only PC-coated prismatic NPs, as observed by TEM. The as-prepared nanoparticles contain on average 86% spheres, 10% prisms, and 4% other, but after one round of sucrose gradient purification (Figure 1C) representative samples contain 43% spheres, 50% prisms, and 7% other shapes. Two rounds of purification were found to be sufficient as the wavelength being monitored was primarily arising from the prisms, minimizing the impact of excess spheres. The CTAB-coated rods (Figure 1B) were synthesized using the method of Sau *et al.*⁴¹ resulting in an average length of 100 nm and average diameter of 15 nm. The pDADMAC-coated octahedral NPs (Figure 1D) were made using the method of Lee *et al.*⁴² giving an average edge length of 50 nm. All samples were cleaned by centrifugation and dispersed in Milli-Q water to remove excess ligand and by-products.

3.2. Fabrication of layer-by-layer assemblies

To make sample preparation as simple as possible, we chose to prepare the samples using drop casting instead of pre-coating the particles and then using dip coating which could be imagined to scale industrially using inkjet printing devices. Typical techniques in preparing layer-by-layer samples involve automated dip coating instruments and optimized agitation.⁴⁴ For our samples, we optimized the incubation time for the drop on the substrate and the polymer. The polymer structures are shown in Scheme 1. The polymers, pDADMAC, PVP, PSS, and PEI, were all freshly prepared at the same concentration of 1 mg/mL in 0.5 M sodium chloride and filtered before drop casting using a 0.1- μ m syringe filter. The pH was not adjusted due to the GNPs being more sensitive to changes in acid/base conditions. The incubation time for the polymer solution was kept constant at 30 min for each of the polymers. After the polymer solution was incubated the sample was rinsed with a stream of Milli-Q water followed by drying with a flow of nitrogen. All polymers were high enough molecular weight to form thin films and thicknesses were measured on glass substrates by cleaning a portion of the polymer and using atomic force microscopy (AFM) to measure the difference in height between the coated and uncoated glass; pDADMAC = 26 ± 4 nm, PVP = 66 ± 8 nm, PSS = 73 ± 1 nm, and PEI = 228 ± 18 nm.

3.3. Characterization of gold nanoparticles and layer-by-layer assemblies

The LSPR of GNPs is sensitive to the RI of its surroundings. To test the binding of the GNPs to the polymers we followed the LSPR of the citrate-capped spheres in real time as polymer solution was titrated in. Figure 2 shows the spectra for each polymer addition (pDADMAC, PEI, PVP, and PSS) and the centroid shift in nanometers as the polymer concentration was increased. pDADMAC shows a moderate change at lambda maximum, some broadening, and a shoulder peak around 650 nm, suggesting particle aggregation is taking place (Figure 2A). DLS reveals a 300% increase in the hydrodynamic radius after addition of the pDADMAC is complete. PEI shows the strongest interaction with the citrate-capped spheres (Figure 2B, 2E). The particles aggregate more and more with each additional titration of PEI and a prominent second peak occurs at 650 nm. DLS shows a 600% increase in size after the PEI addition is complete. PVP and PSS have very little interaction, causing a slight shift in centroid due to minimal particle aggregation (Figure 2C and D, respectively). PVP causes a 4% increase in size to the GNP sample. PVP and PSS have almost no effect on the plasmon wavelength (Figure 2E). The small blue-shift for PSS combined with a trivial (3%) increase in size suggests that a change in the ligand shell such as removal of citrate may explain the

blue shift rather than changes in aggregation state (Figure 2E). This is due to the fact that PSS is the only negatively charged polymer examined and citrate-capped GNPs also having a negative surface charge.

Layer-by-layer assembly using drop casting was optimized for each GNP shape using the four polymers (Scheme 1). No capping of the GNPs was performed but the ligand shell originating from the synthesis is likely to be present from each synthetic method. After depositing a polymer base layer, GNP solutions were added. Each GNP (five in total) and each polymer solution was sequentially drop cast and the films were monitored by UV-vis spectroscopy. After five layers if the OD was not increasing above 0.1 it was determined the GNP/polymer combination was not assembling and that sample was not taken any further. Incubation time was kept constant for the polymer solution at 30 min but varied for the nanoparticle solution. The longer the incubation time the more nanoparticles that were deposited but also the broader the UV-vis spectrum peak. Fifteen minute incubation time for citrate-capped spheres was found to be ideal for minimizing broadening and thirty minutes for the other nanoparticle shapes. Figure 3 shows the comparison between citrate-capped spheres and the two polymers (PEI and PVP) that were successfully assembled into films. The UV-vis spectra were collected for each of the first five layers and then every fifth layer until a high OD at NIR wavelengths was achieved. The OD and wavelength at maximum OD was determined from the UV-vis spectra during deposition.

An increase in OD indicates an increase in the density of nanoparticles, whereas a centroid shift indicates decreased nanoparticle spacing. The addition of a polymer layer should prevent nanoparticle-nanoparticle interaction between layers depending on the thickness of the polymer layer. However, a correlation between OD and red-shifting suggests plasmonic coupling between layers. The citrate-capped sphere/PEI combination reveals a strong correlation between the increase in OD and red-shift with the number of layers (Figure 3A and 3B). As was observed in solution (Figure 2B), the citrate-capped spheres and PEI had the strongest interaction and formed aggregates. In the layer-by-layer assembly each layer was dried before the next layer was drop cast thereby decreasing the chances for polymer and nanoparticle aggregation. However, both polymer and nanoparticle are water soluble and therefore can have interactions at the interface. The particles are less than 100 nm and the dried polymer thicknesses were less than 100 nm except for PEI, which was approximately 230 nm (as measured via AFM). Even at the first layer, the plasmon resonance for the citrate-capped spheres is red-shifted (680 nm) compared to the nanoparticles in solution (520 nm). After 100 layers, the film reached 2.7 OD and a maximum wavelength of 715 nm. The LBL film formed with citrate-capped sphere/PVP combination (Figure 3C) shows a correlation between the increase in OD and red-shift. But after 25 layers the increase in OD and red-shift per layer decreases (Figure 3D). A passivation layer appears to have formed either in the nanoparticle or polymer layer. The OD is approximately 0.8 and the centroid is 630 nm so it does not appear that nanoparticle aggregation is the culprit. PVP in solution did not have a strong interaction with citrate-capped sphere nanoparticles in solution but was strong enough to create sequential layers above 0.5 OD. The lack of charge on PVP is most likely the reason but why the deposition rate changed after 25 layers is not understood. The layer-by-layer process was continued until 100 layers were deposited and an OD of 0.78 at

800 nm was reached. Even though this method takes longer to reach high OD at NIR wavelengths the red-shifting is minimized as compared to PEI.

GNPs with high aspect ratios are of interest in sensor applications because their LSPR wavelength is in the NIR range. Figure 4 shows the OD and centroid measured increasing layer-by-layer assemblies of PC-coated spheres/pDADMAC (Figure 4A), CTAB-coated rod/PSS (Figure 4B), PC-coated triangular prisms/pDADMAC (Figure 4C), and pDADMAC-coated octahedra/PSS (Figure 4D). PC-coated spheres/pDADMAC increased OD most rapidly out of all the samples and only red-shifted approximately 100 nm from the solution centroid 520 to 620 nm for 20 layers. This is most likely due to the PC coating on the spherical GNPs from the synthesis preventing aggregation. This assembly method may be of greatest interest to those looking to make solid state samples quickly and reproducibly. CTAB-coated rod/PSS was the optimal polymer for growing thin films of nanorods. However the OD was less than 0.35 OD after 50 layers and the red-shifting increased rapidly (Figure 4B). After 15 layers a maximum wavelength could not be determined due to the UV-vis spectrophotometer stopping at 900 nm, so the OD was measured at 800 nm. A passivation layer seemed to be forming with this combination as well, but here the GNPs are likely to be the cause due to the high aspect ratio and aggregation. PC-coated prisms/pDADMAC increased with a high correlation to high OD at NIR wavelengths in 35 layers. PC-coated prisms/pDADMAC (Figure 4A) red-shifted less than 30 nm which is the least from of all the different samples tested, and this sample may be of great interest to those looking for applications in the NIR range. pDADMAC-coated octahedra/PSS (Figure 4D) showed a correlation in the increase in OD and red-shift as the number of layers increased. The red-shifting seemed to diminish more than the OD was increasing so NIR wavelengths would have taken longer to reach and this sample was stopped.

Atomic force microscopy (AFM) height images were used to determine the extent of aggregation of nanoparticles that had been deposited on the polymer surfaces after maximum number of layers were achieved (Figure 5). The different shape and size GNPs drop cast were deposited as the last layer in all samples. The citrate-capped spheres/PVP image shows the nanoparticles are encapsulated in the polymer (Figure 5A). The water that disperses the citrate-capped spheres also dissolves the polymer allowing it to interact with the surface. The citrate-capped spheres/PEI image shows similar results as the citrate-capped spheres/PVP, however the interaction is stronger as more nanoparticle encapsulation is observed (Figure 5B). As was shown in Figure 3, there was more red-shifting in the citrate-capped spheres/PEI sample as compared to the citrate-capped sphere/PVP sample. The PC-coated sphere/pDADMAC image indicates interaction and large 100 nm Z-dimension changes and greater than 500 nm X- and Y-dimension changes (Figure 5C). The PC-coated triangular prisms/pDADMAC image (Figure 5D) shows similar indication of good overlap interaction as the PC-coated sphere/pDADMAC image because they both have PC coatings on the GNPs. The CTAB-coated rod/PSS image shows a lower coverage area than all the other samples, but still has good interaction as no individual rods are observed (Figure 5E). The pDADMAC-coated octahedral/PSS image shows similar morphology to the citrate-capped spheres and polymer (Figure 5F). The OD and red-shifting was similar for the pDADMAC-coated octahedral/PSS sample to the citrate-capped sphere/polymer as well. The total height was measured using AFM for each of these samples after cleaning a portion

down to bare glass. The citrate-capped sphere/PEI thickness was measured to be 209 ± 7 nm for the 100 layer sample. The citrate-capped sphere/PVP thickness was measured to be 63 ± 6 nm for the 100 layer sample. The CTAB-coated rod/PSS thickness was measured to be 145 ± 7 nm for the 50 layer sample. The pDADMAC-coated octahedral/PSS thickness was measured to be 374 ± 18 nm for the 35 layer sample. The PC-coated sphere/pDADMAC thickness was measured to be 236 ± 26 nm for the 25 layer sample. The PC-coated prism/pDADMAC thickness was measured to be 291 ± 10 nm for the 25 layer sample. This demonstrates that a hard layer model is not adequate in explaining and understanding these hybrid metal/polymer systems. Comparing the two citrate-capped spheres, PEI afforded the thicker film (209 nm) whereas PVP produced a thinner film (63 nm). This may be due to PEI being a branched polymer with a slightly larger molecular weight (50,000 vs 10,000 g/mol) allowing for better polymer chain entanglement. Next, comparing PSS with CTAB-coated rod (145 nm) and pDADMAC-coated octahedra (374 nm), the rod is thinner even though it has 50 layers compared to 35 layers for the octahedra. This may be due to the aspect ratio of rods being thinner than octahedra, and also may be due to pDADMAC coating making octahedra slightly larger. Lastly, comparing pDADMAC with PC-coated spheres (236 nm) and PC-coated prisms (291 nm), both with 25 layers the difference is minimal most likely due to the PC coating being the same regardless of the prism or sphere shape or size.

3.4. Binding and sensing applications

Prior to assessing the sensitivity of the films to changes in RI, we assessed the sensitivity of each GNP to changes in solution RI for comparison. Figure 6 shows the comparison between citrate-capped and PC-coated spherical GNPs. The LSPR was monitored in real time for each sample as sucrose was titrated in (Figure 6A and B). The centroid was determined from each spectrum and plotted over time (Figure 6C and D). The citrate-capped spheres show a large initial centroid shift at 1 wt% sucrose and significantly less with each addition up to 5 wt% sucrose (Figure 6C). The sensitivity was determined by fitting a line to the centroid versus RI giving a value of 71.6 nm/RIU (RI units). The PC-coated spheres showed a very small change in centroid after each sucrose addition which is due to the PC only coating the core (Figure 6D). The sensitivity of PC-coated spheres toward sucrose in solution was determined to be 14.8 nm/RIU. Another indication the PC-coated spheres are more insulated in solution than the citrate-capped spheres is that the PC-coated sphere spectra are more narrow and red-shifted as compared to the citrate-capped sphere spectra.

The non-spherical shaped GNPs synthesized were also tested with sucrose in solution for RI sensitivity (Figure 7). They all showed higher LSPR sensitivity than the spheres. PC-coated triangular prismatic nanoparticles had a much higher sensitivity than the PC-coated spheres (almost ten times higher) and more than double that of citrate spheres which was to be expected due to the higher aspect ratio. The LSPR of PC-coated triangular prismatic GNPs (Figure 7A) was followed in real time in solution as sucrose was titrated in (1, 2, 3, 4, and 5 wt% final concentration) while stirring. The centroid shift was determined from the spectra over time (Figure 7D) which gave a sensitivity of 145.0 nm/RIU. CTAB-coated rods have the highest wavelength LSPR and are reported to have CTAB bilayer coating the rods.⁴⁵ The LSPR of the rods was monitored in real time in solution as sucrose was titrated while stirring

(Figure 7B). The LSPR of the CTAB-coated rods was the most red-shifted and broadest (highest full width at half-maximum, FWHM) out of all the GNP shapes and sizes and also showed the strongest RI sensitivity (Figure 7E). The sensitivity was determined from the centroid shift versus RI to be 1002.4 nm/RIU (fourteen times greater than citrate-capped spheres). The LSPR of the pDADMAC-coated octahedra were monitored in real time in solution as sucrose was titrated while stirring (Figure 7C). The spectra of the pDADMAC-coated octahedra showed small changes with each sucrose addition, similar to PC-coated spheres but slightly greater, even though pDADMAC-coated octahedra nanoparticles have more edges. Also, octahedra may still have pDADMAC coating the GNPs from the synthesis. The centroid shift (Figure 7F) was acquired from the spectra over time giving a sucrose sensitivity of 51.7 nm/RIU.

With the layer-by-layer samples optimized, we sought to test the sensitivity of the thin film samples to RI changes and also compare to the solution state results to learn about the nanoparticle surface accessibility in the solid state. The solution state has higher degrees of freedom so we expected the solution values to be higher but were surprised to see a big increase in some of the thin film sensitivities suggesting that sucrose permeates into some of the films. Figure 8 shows the LSPR for citrate-capped spheres/PVP and citrate-capped spheres/PEI as sucrose was titrated (5, 10, 15, 20, and 25 wt% sucrose final concentration) with the solid-state sample glued to the side of a cuvette. The citrate-capped sphere/PVP sample red-shifted with each sucrose addition and the centroid shift versus RI gave a sucrose sensitivity of 18.8 nm/RIU (Figure 8, black square). This is surprising because as seen in the AFM image (Figure 5) the citrate-capped sphere/PVP sample seemed to be closest to the surface, so possibly repulsion from the polymer reduces sensitivity as compared to solution state of citrate spheres and sucrose (71.6 nm/RIU). Previous efforts at immobilizing spheres using a combination of PEI, PSS, and poly(allylamine hydrochloride) showed an 85 nm/RIU value whether in solution or immobilized.⁴⁶ This suggests that PVP blocks access to the nanoparticle surface, while in our experiments PEI led to a higher sensitivity (135.1 nm/RIU) (Figure 8, red circle), possibly due to some stripping of the citrate coating or the creation of hotspots between the particles.^{2,7} The AFM image showed more aggregation and PEI has more branching in the polymer backbone for hydrogen bonding with sucrose. Also, the citrate-capped spheres/PEI sample had a higher OD which should not affect the results because it is a shift in the centroid. Further work in making samples that are closer in OD will help in understanding these differences.

The layer-by-layer samples prepared with non-spherical GNP shapes were tested for sucrose sensitivity with some showing increased sensitivity compared to solution. Figure 8 shows results of the LSPR monitoring with CTAB-coated rods/PSS (black square), PC-coated triangular prisms/pDADMAC (red circle), pDADMAC-coated octahedra/PSS (green triangle, up), and PC-coated spheres/pDADMAC (blue triangle, down) samples glued inside a cuvette as sucrose was titrated in and stirred. The sensitivities were determined to be 52.5 (CTAB-coated rod/PSS), 31.8 (PC-coated prism/pDADMAC), 68.6 (pDADMAC-coated octahedra/PSS), and 59.8 nm/RIU (PC-coated sphere/pDADMAC). In comparison to the solution state, the CTAB-coated rod sensitivity was 19.1 times higher in solution (1002.4 nm/RIU) and the PC-coated prisms were 4.6 times higher in solution (145.0 nm/RIU), suggesting hindered access within the multi-layers. The CTAB-coated rods have a high aspect ratio, may pack

together tightly resulting in lowered sensitivity in the layer-by-layer thin film. The PVP films reduced this sensitivity 3.8 fold. Different self-assembly techniques could help in increasing the degrees of freedom in thin film samples.⁴⁷ The PC-coated prisms showed good coverage with pDADMAC in the AFM image and their UV-vis spectra however showed little aggregation. Thick coverage with a sucrose impermeable polymer may explain why these prisms were much less sensitive than monolayers of prisms affixed using PEI, PSS, and poly(allylamine hydrochloride).⁴⁶

In contrast, the pDADMAC-coated octahedra were 1.6 times more sensitive in the film than they were in solution (51.7 nm/RIU) and the PC-coated spheres were 4 times more sensitive in the film than in solution (14.8 nm/RIU). In both of these cases the ligand may be displaced during the LBL assembly process. The pDADMAC-coated octahedra showed similar density in the AFM images as the citrate spheres. The sucrose sensitivity is slightly higher in the layer-by-layer thin film samples as compared to the solution state which is similar to but not as drastic as the citrate-capped spheres/PEI. There does not appear to be a problem with sucrose and polymer interactions. The PC-coated spheres are basically citrate spheres and now in layer-by-layer thin film samples should behave similarly. As shown in the UV-vis spectra however the PC-coated spheres did not aggregate with each sequential layer like the citrate-capped spheres did. Also, it only took 25 layers to reach high OD instead of 100 layers. However, the AFM image for PC-coated spheres/pDADMAC showed complete coverage. The increased sucrose sensitivity in the thin film as compared to the solution state cannot be attributed to the pDADMAC because in the prism case it was suggested it may be the culprit in lowered sucrose sensitivity. The citrate-capped spheres in solution showed a sucrose sensitivity (71.6 nm/RIU) that is similar to the PC-coated sphere/pDADMAC (59.8 nm/RIU) which seems to point to the PC being removed in all the rinsing when assembling the layer-by-layer thin film so that it acts similar to the citrate sphere. This would strengthen the argument that the citrate-capped sphere/PVP sensitivity being lower because of PVP and the citrate-capped sphere/PEI sensitivity being higher due to PEI.

The film that achieved the highest OD at 100 layers, PEI with citrate spheres, also showed the highest sensitivity to sucrose. In contrast, the same particles, prepared in a thin film using PVP, resulted in much lower sensitivity and less of an increase in OD. The increase suggests that treatment with PEI either strips citrate ligands from the surface of the gold to increase sensitivity or that hot spots are created within the nanoparticle aggregates that have higher sensitivity than the original GNPs. In overall sensitivity, the PEI/citrate spheres had the highest sensitivity to increased RI. However, in other cases, these same citrate GNPs lost sensitivity during the LBL process with PVP. The asymmetric nanoparticles have more to lose, as their high sensitivities are often dependent on analyte access to specific regions of the GNP surface. The prisms and rods both showed reduced sensitivity in thin films while the octahedra showed enhanced sensitivity. Different packing densities likely explain these differences. Polymer choice affects the GNP ligand shell, the packing density within the LBL film, and the accessibility and possible creation of hot spots. While no single, universal design principle can be derived from the data, in practice the ideal polymer for density may not be the ideal polymer for analyte access. Combinations of polymers, not explored in this work, may provide the best method to ensure both high density and analyte access.

4. Conclusions

The development of efficient techniques for making thin films with tailored and controlled parameters from GNPs is critical for the realization of practical devices. The size, shape, and charge of gold nanoparticles alter their intrinsic optical properties but also effect how they assemble.^{11, 47} Nanoparticle shape influences interactions between polymers and GNPs as the intersections between facets on the surface of a GNP has a lower density of surface coating and the resulting void can be filled by wetting of the polymer, thereby preventing aggregation.⁴⁸ Therefore, the optimal polymer for assembling asymmetric nanoparticles is expected to differ from that which is ideal for spheres. We found that PSS was the optimal polymer for nanorod and octahedra assembly while PEI was optimal for citrate spheres. The simplest explanation, however, is that differences in nanoparticle surface charge as a result of the different synthetic methods dominated over shape interactions. Furthermore, when comparing different GNP shapes synthesized under similar conditions, pDADMAC was found to be optimal polymer for both spheres and prisms, further supporting the importance of ligand interactions in polymer optimization.

The thickness of 25 to 100 layers obtained here surpasses previous reports and with optical densities ranging from 0.5 to 3.0 at NIR wavelengths these methods will extend the utility of these films for catalysis and sensing applications. This is the first report of LBL assembly of octahedra or prisms and previous attempts at nanorod assembly by LBL were limited to four layers.³⁵ This greatly extends the ability to prepare dense NIR active thin films. Furthermore this approach minimizes the red-shift seen with each layer for octahedra and prisms, allowing for the assembly of many layers while maintaining absorbance close to that of the original nanoparticles. The solution and solid-state sensitivities were also studied leading to a better understanding of analyte access to the active surface, which is important for a variety of device applications.

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Figure 1. TEM images of synthesized GNPs; PC-coated spheres (A), rods (B), prisms (C), and octahedral (D). Scale bars = 100 nm.

Figure 2.

The centroid shift was measured in solution for citrate spheres and each polymer; pDADMAC (A), PEI (B), PVP (C), and PSS (D). Final polymer concentrations of 20, 40, 60, and 80 ng/mL were added each 10 min and scans were collected every second. Plot of polymer sensitivity for citrate-capped spherical GNPs obtained from the change in centroid versus final polymer concentration (E).

Figure 3.

UV-vis spectra showing layer-by-layer assembly for citrate-capped spheres/PEI (A and B) and citrate-capped spheres/PVP (C and D) along with the OD and centroid for each layer taken from the UV-vis spectra; filled black square = OD and open blue circle = wavelength.

Figure 4.

The OD and centroid were measured for PC-coated spheres/pDADMAC (A), rod/PSS (B), prism/pDADMAC (C), and octahedra/PSS (D) for each layer from the UV-vis spectra characterization showing an increase in particle density and red-shifting; filled black square = OD, open blue circle = wavelength.

Figure 5.

Atomic force microscopy (AFM) images of layer-by-layer samples show polymer and gold particles are fully entangled; citrate-capped sphere/PVP (A), citrate-capped sphere/PEI (B), PC-coated sphere/pDADMAC (C), prism/pDADMAC (D), rod/PSS (E), and octahedra/PSS (F).

Figure 6.

The localized surface plasmon resonance (LSPR) was monitored for citrate-capped (A and C) and PC-coated (B and D) spherical GNPs in solution as sucrose (1, 2, 3, 4, and 5 wt%.) was added. The sensitivity was determined from the centroid shift to be 71.6 and 14.8 nm/RIU, respectively.

Figure 7.

The localized surface plasmon resonance (LSPR) was monitored for prism (A and D), rod (B and E), and octahedral (C and F) in solution as sucrose (1, 2, 3, 4, and 5 wt.%) was added. The sensitivity was determined from the centroid shift to be 145.0, 1002.4, and 51.7 nm/RIU, respectively.

Figure 8.

The localized surface plasmon resonance (LSPR) was monitored for citrate sphere/PVP (filled black square), citrate sphere/PEI (filled blue circle), for rod/PSS (filled red rod), prism/pDADMAC (filled green triangle), octahedra/PSS (open black hexagon), and PC sphere/pDADMAC (open red circle) sample as sucrose (5, 10, 15, 20, and 25 wt%.) was added. The sensitivity was determined from the centroid shift to be 18.8, 135.1, 52.5, 31.8, 68.6, and 59.8 nm/RIU, respectively.

Scheme 1.

Polymer structures used for GNP layer-by-layer assembly; poly(diallyldimethylammonium chloride) (pDADMAC), polyvinylpyrrolidone (PVP), poly(sodium 4-styrene sulfonate) (PSS), and polyethylenimine (PEI).