



Regular Article

Polymer mediated layer-by-layer assembly of different shaped gold nanoparticles

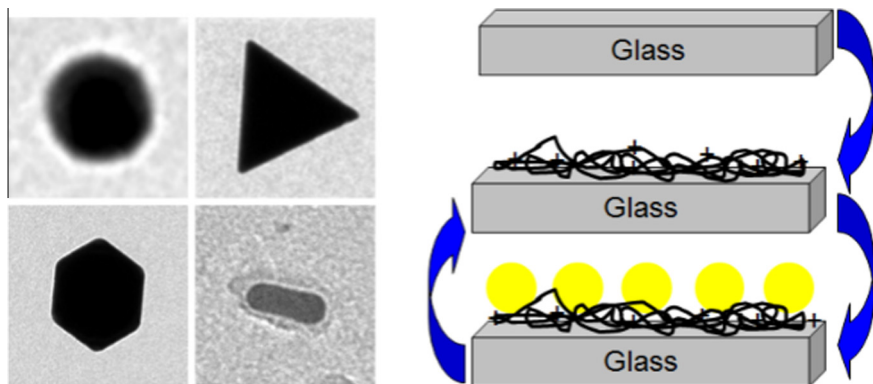


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GRAPHICAL ABSTRACT



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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/refractive index units (RIU) and films ranged from 18.8 to 135.1 nm/RIU suggesting reduced access to the GNPs within the films.

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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

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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], polyhedra [20], and stars [21] 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 explored [35] 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 loading 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

2.1. Materials

L- α -Phosphatidylcholine (Type IV-S, $\geq 30\%$ 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, hexadecyltrimethylammonium bromide (CTAB) was from B-Biosciences, and hydrogen tetrachloroaurate(III) hydrate (99.9% Au, HAuCl₄·H₂O) and hydrogen tetrabromoaurate (III) hydrate (99.9% Au, H₂ABr₄·H₂O) 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 × 25 × 1 mm).

2.2. 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

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