

Supporting Information

Layer-by-Layer Assembly of Heterogeneous Modular Nanocomposites

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Materials and Methods

Gold nanoparticles. The gold colloid dispersion was prepared as previously described in the literature (ref 17). Briefly, a 100 mL of stock Au(III) aqueous solution was prepared from 1.00 g tetrachloroauric acid (HAuCl₄, ≥99.9% purity, Aldrich) in an amber volumetric flask. The stock solution then was aged for one month in the dark.

Before preparing the Au colloid, an Erlenmeyer flask and a Teflon® stirbar were cleaned by soaking in *aqua regia* (3:1 mixture of HCl and HNO₃) for 20–30 min, followed by a triple rinse in deionized water, and drying overnight in an oven at 110°C. *Caution: Aqua regia solutions are extremely corrosive and may result in explosion or skin burns if not handled properly.* A mixture of 1 mL of the stock Au(III) solution and 100 mL of deionized water was added to the clean flask, the flask then was covered loosely with a watch glass and the stirred contents were brought to a gentle boil. A 2.5 mL aliquot of an aqueous solution containing 1% wt. trisodium citrate (99%, Aldrich) was quickly added to the stirred contents of the flask. After formation of a clear, cherry red sol, it was gently boiled for an additional 10 min to complete the reduction, then allowed to cool to room temperature covered with the watch glass. The stirbar was removed, deionized water was added to return the volume to 100 mL, and the flask was capped tightly and stored for later use.

Substrate cleaning. Two types of substrates were used for LbL assembly: polished fused silica slides (Dell Optics, Inc.) and single-side-polished Si wafers (n-type, As-doped, <100> orientation, Recticon Corp.) For initial cleaning, Si wafers and fused silica slides were placed in a slotted Coplin jar and covered with a 1:1 v/v mixture of methanol and concentrated HCl. The jar was loosely capped and allowed to stand for 45 min in a fume hood. Then the cleaning solution was drained and the substrates were thoroughly rinsed with deionized water. After draining the water, the substrates were covered with concentrated H₂SO₄ and allowed to stand for 45 min in the loosely capped jar. The sulfuric acid then was decanted away and the substrates were thoroughly rinsed with deionized water.

Substrate modification. After cleaning, the substrates were modified by chemisorption of EDA (*N*-(2-aminoethyl)-*N*-3-aminopropyltrimethoxysilane, Gelest, Inc.) The EDA solution was prepared by adding 2 mL of EDA to 200 mL of deionized water, mixing to dissolve the EDA, and then adding 240 μL of glacial acetic acid. The clean substrates were covered with the EDA solution for 30 min at room temperature then thoroughly rinsed with deionized water. Immediately after the final rinse, the substrates were dried in a filtered N₂ gas stream, baked 6–8 min in an oven at 110–120°C, cooled, and stored in plastic containers.

Polyelectrolyte solutions. A stock solution of 1.00 M NaCl (aq) was prepared in a volumetric flask by dissolving 58.44 grams of NaCl in 1 L of deionized water. Polyallylamine hydrochloride (PAH, mol. wt. 56000 g/mole, Aldrich) and

sodium polystyrenesulfonate (PSS, mol. wt. 70,000 g/mole, Aldrich) were chosen as the polyelectrolytes for LbL assembly. The PAH solution of 2 mg/mL concentration was prepared in a volumetric flask by dissolving 2.00 grams of PAH in 1 L of the stock NaCl (aq) solution. The PSS solution of 2 mg/mL concentration was prepared in a volumetric flask by dissolving 2.00 grams of PSS in 1 L of the stock NaCl (aq) solution.

To investigate the effects of salt counterions on the LbL assembly of PAH and PSS, several polyelectrolyte solutions were prepared with a combination of NaCl and “guest” salts. The total ionic strength of all the mixed-salt solutions was maintained at 1.00 M. Keeping NaCl as the majority salt in all the mixtures helped to prevent solubility and aggregation of polymers from dominating the observed effects of changing the counterion content.

By dissolving 46.7 g of NaCl and 6.0 g of MgSO₄ (99% purity, Aldrich) in deionized water, 500 mL of a stock solution containing 0.10 M MgSO₄ and 1.6 M NaCl was prepared in a volumetric flask. In separate 500 mL volumetric flasks, stock polyelectrolyte solutions were prepared by dissolving 2 g of PAH or PSS in deionized water. Equal volumes of the stock solutions were mixed to prepare the PSS and PAH dipcoating solutions, containing 2 mg/mL of the respective polymers and 0.05 M MgSO₄ in 0.80 M NaCl (aq). No precipitation was observed when preparing the PSS dipcoating solution. In contrast, the salt stock solution had to be slowly added to the well-stirred PAH stock solution to completely dissolve the precipitate that was forming during the mixing and to produce the final PAH dipcoating solution that was clear and stable.

Additional dipcoating solutions prepared with guest salts were based on aqueous 0.05 M MgCl₂ + 0.85 M NaCl, 0.05 M Na₂SO₄ + 0.85 M NaCl, 0.05 M NaH₂PO₄ + 0.95 M NaCl, and 0.05 M NaF + 0.95 M NaCl mixtures.

LbL assembly. For LbL assembly of nanocomposites, the EDA-modified substrates were loaded onto a glass carousel and dipcoated (following the sequence specified for each set of samples) in the PSS and PAH solutions and in the Au sol. The dipcoating times were 25 min in the PSS and PAH solutions and 18.5 h in the Au sol. Samples were rinsed and dried in a N₂ gas stream between dipcoating cycles. To minimize dilution and contamination during the dipcoating process, the PAH and PSS solutions were replaced after depositing 6–8 polymer layers and fresh aliquots of Au sol were used for each deposition of Au NPs. The LbL assembly was monitored by following the evolution of the UV-vis spectra measured from periodically withdrawn witness samples on fused silica slides (after carefully etching away with *aqua regia* the assembled film from one face of each slide).

Rinsing protocols. Polyelectrolyte layers freshly deposited from some of the mixed-salt dipcoating solutions appeared to interact with deionized water (e.g., by producing cloudiness emanating from the surface) when rinsed immediately after

dipcoating. Accordingly, two types of rinsing protocols were used to check for the effects of the rinsing solution.

The standard *water rinse* protocol included three rinsing steps (ca. 5 min each) in separate glass beakers. Each beaker was filled with a copious amount of deionized water immediately before each rinsing step and covered with a watch glass to avoid contamination during rinsing.

The alternative “salt rinse” protocol started with a first rinse in the blank mixed-salt solution of the same composition that was used to prepare the corresponding dipcoating solution (e.g., 0.05 M MgSO_4 + 0.80 M NaCl). A second rinse in 1.0 M NaCl solution was then followed by a final rinse in deionized water.

LbL assembly sequences. The majority of the modular nanocomposites in this work were assembled following the same general sequence denoted Si-EDA/[(PSS/PAH)₄/Au/PAH]₄. The first term in this notation identifies the substrates, which were Si wafers for the main samples analyzed in this work. The second term denotes the EDA modification of the Si wafer substrates. The following expression denotes the modular structure of the nanocomposites. A combination of two modules—a polyelectrolyte multilayer (PSS/PAH)₄ and PAH-capped Au nanoparticle module—is repeated four times to produce the full structure. For some samples, the compositions of the dipcoating solutions were varied for the different [(PSS/PAH)₄/Au/PAH] subunits in the sequence.

Several nanocomposite samples were prepared with an additional polyelectrolyte module [(PSS/PAH)₄ or with a (fifth) full [(PSS/PAH)₄/Au/PAH] subunit on top of the standard sequence.

Samples on fused silica slides were prepared alongside the samples on Si wafers, thus following the same assembly sequences. Witness samples were withdrawn, typically after completing a [(PSS/PAH)₄/Au/PAH] subunit, for monitoring the deposition by UV-vis spectroscopy measurements.

Control samples of polyelectrolyte multilayers without Au nanoparticles were prepared to evaluate the composition of the polyelectrolyte subunits deposited from different dipcoating solutions. Most of these samples included 20–28 (PSS/PAH) bilayers, with a few shorter sequences prepared to investigate the initial stages of the LbL assembly.

XPS. The composition of polyelectrolyte multilayers and nanocomposites was characterized quantitatively by x-ray photoelectron spectroscopy (XPS). The XPS data were acquired in a commercial instrument equipped with a microfocused monochromated Al K α x-ray source, a hemispherical electron energy analyzer, an automated sample positioning stage, and a CCD camera for viewing the calibrated analysis position directly through the analyzer lens. The standard analysis spot of ca. 400×600 μm^2 was defined by the microfocused x-ray source. The energy of the monochromated Al K α x-ray source was automatically calibrated and maintained at 1486.6±0.2 eV. The binding energy (BE) scale of the analyzer was automatically calibrated and verified based on <50 meV deviations of the three standard BE calibration peaks from their standard values (ref 44): 83.98 eV for Au 4f_{7/2}, 368.26 eV for Ag 3d_{5/2}, and 932.67 eV for Cu 2p_{3/2}. Spatially uniform charge correction was provided by a dedicated system that directed collinear beams of low-energy (<10 eV) electrons and Ar⁺ ions onto the sample (ref 36). The raw BE values in each dataset were corrected by ±1.0 eV to place the reference main C 1s peak at 285.0 eV (ref 36); this BE correction was verified on samples that contained Au nanoparticles by observing the Au 4f_{7/2} peak at 84.0 eV (ref 44).

The XPS measurements were performed at room temperature in an ultra-high vacuum analysis chamber with the base pressure

<5×10⁻⁹ mbar; the charge neutralization device produced ca. 2×10⁻⁷ mbar partial pressure of Ar during measurements. High-resolution elemental XPS data in Si 2p, S 2p, C 1s, O 1s, and N 1s regions were acquired with the analyzer pass energy set to 20 eV (corresponding to energy resolution of ca. 0.5 eV) and the step size set to 0.15 eV. Additional high-resolution scans were performed in regions corresponding to elements (including Au and salt counterions) detected in wide survey scans. All the spectra were acquired in normal emission with an analyzer collection angle of ca. 30°.

Gentle sputtering with a beam of Ar⁺ ions was used to investigate the subsurface composition of several samples (beam energy 200 eV, beam current 1 μA , rastered over an area of ca. 4×2 mm²). Systematic sputter depth profiling was not performed because during test attempts apparent strongly preferential sputter yields were observed for the main elements of the PAH and PSS polymers.

High-resolution elemental spectra were quantified using two commercial software packages: Avantage (Thermo Fisher Scientific, Inc.) and Unifit (ref 37). The standard “atomic %” elemental compositions were quantified using calibrated analyzer transmission functions, Scofield sensitivity factors (ref 38), and effective attenuation lengths (EALs) for photoelectrons; EALs were calculated using the standard TPP-2M formalism (refs 36, 39–41).

Results

Mg detection by XPS. With excitation from an Al K α x-ray source, the primary Mg 1s peak potentially overlaps with Cl_{LMM} Auger features in the 1300–1310 eV BE range. Cl is the major component of all the dipcoating solutions in our study and is incorporated in almost all of the LbL assemblies. Accordingly, we systematically evaluated the features in the 1300–1310 eV BE range for any potential Mg 1s contributions, in addition to the expected Cl features.

The expected total intensity of the Cl Auger peaks was empirically estimated based on the total intensity observed in the 1300–1310 eV BE range when various amounts of incorporated Cl have been identified based on the main Cl 2p peak (Figure 3b). As expected, we found a stable empirical “Auger sensitivity factor” from several such measurements, which then was used to estimate the expected Cl Auger intensity for samples with possible presence of Mg and Cl.

In all cases, the upper limit on the Mg concentration was <0.1 atomic %, corresponding to concentrations typically suppressed by a factor of 100–1000 relative to the respective concentrations of N. The Mg incorporation thus was determined to be insignificant in terms of either the composition or charge balance in our LbL assembled samples.

As positive controls, Mg concentrations as low as 0.3 atomic % have been detected in samples specially prepared without Cl, confirming the high sensitivity of XPS for detecting Mg.

Finally, the features in the 1300–1310 eV BE range were observed to disappear after a short etch by 200 V Ar⁺ ions. The removal of the polymer material under these conditions has been previously estimated to be <0.1 nm (ref 36). Accordingly, any Mg present in the subsurface region of the sample would not have been removed. Auger features, however, are sensitive to polymer *damage* by Ar⁺ ions and thus can disappear even when only minimal physical etching occurs.

UV-vis peaks. In Figure S1a, the absorbance peak at ca. 225 nm includes contributions from PSS and Au NPs, whereas the plasmon feature at 500–650 nm is due entirely to the Au NPs.

Spectra in Figure S1a are for slides that were etched by *aqua regia* on one side to remove the deposited film, i.e., the absorbance features in Figure S1a correspond to a single pass through the films of the specified composition. For comparison, Figure S1b shows the spectrum for a control slide without Au NPs, which was not etched by *aqua regia* and thus shows twice the absorbance of a (PSS/PAH)₂₈ polyelectrolyte multilayer.

Comparing the spectra in Figures S1a and S1b provides an estimate of the relative contributions from PSS and Au NPs to the absorbance at ca. 225 nm. Half the absorbance in Figure S1b (ca. 0.75) is the estimate of the PSS contribution. In the equivalent [(PSS/PAH)₄/Au/PAH]₄ composite film, the total absorbance at 225 nm is 2.034, indicating that the contribution at 225 nm from the four modules of Au NPs is at least ca. 1.28.

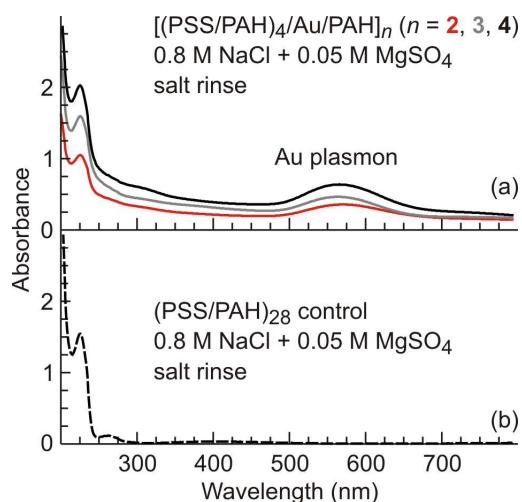


Figure S1. UV-vis spectral signatures of LbL assembly of modular nanocomposites. (a) Samples on fused silica substrates were withdrawn for UV-vis measurements after the deposition of each Au NP module (indicated by color coding). The dipcoating solutions contained 0.05 M MgSO₄ in 0.80 M NaCl, the 3-step salt rinse was performed after deposition of each layer. (b) Control sample for which the LbL assembly sequence was the same as in (a) but with Au NP layers replaced by PSS.