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Stability of anti-reflection coatings via the self-assembly encapsulation of silica nanoparticles by diazo-resins

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ABSTRACT

A modified silica nanoparticle (MSNP) solution was formed by the encapsulation of negatively charged silica nanoparticles by the UV-crosslinkable polycation oligomer diazo-resin (DAR). Appropriate DAR encapsulation concentrations were determined by use of zeta-potential and dynamic light scattering measurements. The MSNPs were used in conjunction with poly(styrene sulfonate) (PSS) to grow homogenous ionic self-assembled multilayer anti-reflection coatings. Stability was induced within the films by the exposure of UV-irradiation that allowed for crosslinking of the DAR and PSS. The films were characterized by UV/vis/IR spectroscopy and field emission scanning electron microscopy. The transmission and reflection levels were $>98.5\%$ and $<0.05\%$, respectively. The refractive indices resided in the 1.25–1.26 range. The solvent stability was tested by sonication of the films in a ternary solvent (H_2O/DMF/$ZnCl_2$ 3:5:2 w/w/w).

1. Introduction

Anti-reflection coatings (ARCs) are commonly used to reduce substrate reflection, while maximizing transmission, in the visible wavelength range of incident light. Along with a decrease in loss of transmitted light, ARCs diminish glare created by high levels of reflected light. ARCs must fulfill two conditions to exhibit zero reflectance due to destructive interference (1) OT$=\lambda/4$ and (2) $n_c = \sqrt{n_1 n_2}$ where OT is the optical thickness of the coating (product of the physical thickness and refractive index), λ is the desired wavelength in nm, n_c is the refractive index of the coating, and n_1 and n_2 refer to the refractive indices of the media on either side of the coating. Condition (1) creates a π-phase shift between light reflected off the underlying substrate and the light reflected off the coating, resulting in destructive interference. Condition (2) ensures that the amplitudes of the reflected electromagnetic waves from the upper and lower ARC coating surfaces are equal. In the commonplace example that the substrate is composed of glass ($n=1.50$) and the surrounding medium is air ($n=1.0$), the refractive index of the coating should be $n_c=1.22$. Condition (1) is far less stringent to accomplish, as modern methods of film growth can precisely control thickness, whereas condition (2) requires control on the composition of the coating, which is not as variable, comparatively. Single-layer ARCs consist of one transparent dielectric material for low reflectance in a narrow range of wavelengths. MgF_2 is typically used for single-layer ARCs on glass due to its low index of refraction at $n=1.38$. At this refractive index value, MgF2 ARCs reduce the reflectance on a glass substrate from approximately 4–1.2% per surface.

A wide range of deposition techniques have been utilized for ARCs including sol–gel synthesis [1,2], nano-imprint lithography [2,3], plasma-enhanced chemical vapor deposition[4], e-beam evaporation[5], spin coating[6], and chemical etching [7]. Although these methods feature a range of pros and cons, the most common drawbacks relate to high cost and complexity in growth (especially for concave or flexible substrates). Layer-by-layer ionic self-assembled multilayers (ISAMs) address these issues due to the versatility of deposition and their relatively inexpensive nature. The formation of ISAM films relies on electrostatic attraction, hydrogen bonding, and secondary forces and occurs through alternating immersion of a charged substrate into oppositely-charged polycation and polyanion solutions. Adsorption of each individual layer is self-terminated (typically within a few minutes) by completion of the charge reversal. Films can be grown uniformly and homogenously while the thickness can be easily controlled through the number of bilayers (pair of oppositely-charged layers). The technique was originally published by Iler [8], who presented growth of films of oppositely-charged colloidal solutions and the effect of the films thickness to the corresponding interference fringes. This approach was expanded upon by Decher [9] many

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Abbreviations: MSNP, modified silica nanoparticle; DAR, diazo-resin; ARCs, anti-reflection coatings; RCP, randomly closed packed; ISAMs, ionic self-assembled multilayers

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years later, in which anionic and cationic amphiphile solutions were used to construct a layer-by-layer film. Decher's work laid the foundation for similar films to be created with various other materials including biological compounds [10–13], polyelectrolytes [10–12,14,15], and nanoparticles [13,15,16].

As research on inorganic nanoparticles continues to grow, their applications have spread into catalysis [17–19], biomedical [20–22], electronic [23–25], and optical [26–28], as well as several others. In each of these applications, nanoparticles are useful for their large surface area to volume ratio and dense packing. These properties are also valuable for fabrication of high-quality ARCs. Rubner and colleagues have demonstrated ARCs from layer-by-layer films of SiO_2 nanoparticles and a polycation [29] as well as two different types of nanoparticles [30]. In the former case, they demonstrated mechanical stability of the films through calcination. They have also demonstrated broadband ARCs through multilayer stacks of high and low refractive index layers incorporating TiO_2 and SiO_2 nanoparticles, respectively [31]. Our group [26] has also demonstrated ARCs of ISAM films of poly(allylamine hydrochloride) (PAH) and silica nanoparticles (SiO_2 NPs). The porosity established within the films is directly related to the diameter of the SiO_2 NPs and the corresponding randomly closed packed (RCP) structure. This allows a refractive index near the ideal value for a glass–air interface, determined by the weighted average of that of the SiO_2 NPs and the void space between them. The average refractive index of the film ranged from approximately 1.15–1.45. Three different diameter SiO_2 NPs were examined, and the films constructed with the 45 nm SiO_2 NPs yielded the most effective anti-reflection as their refractive index resided in the range of 1.25–1.35, quite near to the ideal value of 1.22. The films' porosity ranged from 30% to 45%, inversely related to the refractive index of the film. While the porosity is critical to yielding a refractive index for the film near the ideal value, it also significantly weakens the stability of the film both mechanically and in interaction with polar solvents and strongly charged solutions.

The incorporation of the photo-curable crosslinking oligomer, diazo-resin (DAR) 4-diazodiphenylamine/formaldehyde condensate hydrogen sulfate into ionically bonded layer-by-layer films is a promising approach for increasing film stability. DAR is a polycation that allows for the conversion of ionic to covalent bonding with various negatively charged functional groups, by the decomposition of its diazonium group under UV irradiation. Cao et al. [32] placed DAR *in situ* with several polyelectrolyte complex solutions containing sulfonate groups (e.g. PSS, PES) and carboxylic acid groups (e.g. PAA, PSPA, PSPM). They performed crosslinking by photoreaction and thermal methods, which demonstrated resistance to decomposition by ternary solvents. The ternary solvents involved water, DMF, and a salt at a common ratio. Three different salts included in the solvent, LiCl, NaSCN, and $ZnCl_2$, were all shown to be effective at dissolving polyelectrolytes that were not crosslinked. The use of $ZnCl_2$ in the ternary solvent mixture has become a standard means for examining the crosslinking in polyelecytrolyte films. Sun et al. expanded upon the production of covalently stable ISAM films via the polycation of DAR and various polyanions including PSS [33] and PAA [34], as well as porphyrins [35]. Fu et al. [36] and Zhang et al. [37] functionalized nanoparticles to develop ISAM films with DAR as the polycation. In all cases, the films were reported to have increased film stability to solvents after crosslinking.

In this report we demonstrate the encapsulation of SiO_2 NPs with DAR by self-assembly to form a polycation. With a solution of this polycation and a PSS polyanion solution, ISAM films were constructed on glass substrates that were visibly homogenous across the surface. The films displayed peak transmittance values similar to those of Yancey et al. The films exhibit covalent stability in the bulk of the film (crosslinking between DAR and PSS) and on the substrate surface (crosslinking between DAR and grafted sulfonated silanes). The films were characterized by UV–vis spectrometry, scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements.

2. Experimental

2.1. Materials

4-Diazodiphenylamine/formaldehyde condensate hydrogen sulfate (DAR) (M_w=2,800) was graciously donated by Secant Chemicals. SNOWTEX ST-20L SiO_2 NP solution was purchased from Nissan Chemical, composed of 45 nm average diameter particles, with a concentration of 20 wt%. Poly(styrene sulfonate) (PSS) (M_w=70,000) was purchased from Polysciences Inc. The aqueous solutions were developed and diluted with ultrapure de-ionized water (18 MΩ cm resistivity) (DI water). 95% (3-mercaptopropyl) trimethoxysilane (MPTS) solution was purchased from Sigma-Aldrich. Other reagents used for glass microscope slide preparation were of analytical grade and unaltered for use.

2.2. Instrumentation

The ISAM films were fabricated with a programmable automated immersion system from nanoStrata, Inc. The MSNP films were UV irradiated by a Kinsten KVB-30 exposure unit, which had six 20 W UV fluorescent bulbs. A Zetasizer nanoZS (Malvern Instruments) operating at a fixed angle of 173° and 633 nm wavelength was utilized for ζ-potential and dynamic light scattering (DLS) measurements. The optical transmission, reflection, and absorption spectra were recorded by a Perkin Elmer Lambda 950 UV/VIS and a Filmetrics F10-RT-EXR spectrophotometer. The physical thickness measurements were performed with a Veeco DekTak 150 Stylus Profilometer with a 2.5 μm tip radius stylus and an application of 1 mg force. A LEO 1550 field emission scanning electron microscope (FESEM) unit at an accelerating voltage of 5 kV was used to characterize the morphology.

2.3. Solution formation

The SiO_2 NPs were encapsulated with DAR while in solution, to allow for the SiO_2 NPs to be involved with the crosslinking reaction between DAR and PSS. The encapsulated SiO2 NPs are designated modified silica nanoparticles (MSNPs). In order to identify the conditions under which the SiO_2 NPs are fully covered with DAR without substantial excess remaining in the solution, a range of DAR concentrations were added to the SiO_2 NP solution and mixed for 12 h. The solutions were sonicated for a total of 80 minutes to induce maximum dissolution of potential agglomerates. Schematic representation of the self-assembly directly onto the particles is shown in Fig. 1(a–f).

Through encapsulation, two conditions are satisfied: (1) conversion of the anionic SiO_2 NP solution to cationic (necessary for ionic film growth with a polyanion) (2) the DAR polyelectrolyte chains, on the surface of the MSNPs, could be used for crosslinking with the sulfonate groups of the polyanion PSS after film construction. In this manner, self-assembled encapsulation was carried out in a three-dimensional (3D) architecture in solution, forming nanocomposite shells to later be used in conventional two-dimensional (2D) layer-by-layer film growth. An example of a comparable nanocomposite synthesis was shown by Keller et al. [38], and Pastoriza-Santos et al. [39] produced a similar solution with ZrO_2 nanoparticles encapsulated by DAR. After the encapsulation process, ζ-potential and dynamic light scattering (DLS)