Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Bio-Inspired Iridescent Layer-by-Layer Assembled Cellulose Nanocrystal Bragg Stacks

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Experimental

1. Materials

Cationic solutions were prepared by adding 0.1 wt% of branched polyethylenimine (PEI) (Aldrich, St. Louis, MO) (MW ~ 25,000 g mol^{-1}), or 1 wt% of colloidal silica (SiO_2) (particle size 12 ± 2 nm) (trade name Ludox CL) (Aldrich, St. Louis, MO), into 18.2 MΩ deionized water. The pH of PEI and SiO_2 were adjusted to 10 and 4, respectively, by adding 1.0 M hydrochloric acid (HCl). Anionic solutions were prepared by mixing 1 wt% vermiculite (VMT) (Aspect ratio ~1100) (trade name Microlites 963++) (Specialty Vermiculite Corp., Cambridge, MA), or 0.1 wt% cellulose nanocrystals (CNCs) (mean aspect ratio ~18, with lengths of 109 ± 34.5 a diameter of 6.0 ± 1.9), into deionized water. CNCs were produced using sulfuric acid hydrolysis based on the method used by Clift et al.[1] CNC suspensions were adjusted to pH 7 using 0.1 M NaOH. VMT solutions were set for 24 hours before use, then the supernatant was used at its natural pH (~7.5).

2. Layer-by-layer deposition

Single-side-polished (100) silicon wafers (University Wafer, South Boston, MA) were used as substrates for ellipsometry and scanning electron microscopy (SEM). Fused quartz slides (Structure Probe Inc., West Chester, PA) were used to measure the optical reflection from the films. Both silicon wafers and quartz slides were rinsed with deionized water and methanol before use, then plasma-treated with an ATT0 Plasma Cleaner (Thierry Corp., Royal Oak, MI). Plasma treatment improves adhesion of the first polyelectrolyte layer by oxidizing the substrate surface.[2] Each substrate was first dipped into the PEI solution for 5 minutes, followed by rinsing with deionized water for 30 seconds and drying with a stream of filtered air. After the first positively-charged layer was adsorbed, the substrate was dipped into the VMT solution for another 5 minutes, followed by another rinsing and drying cycle. Starting from the second bilayer deposition, the remaining layers were deposited using one minute dip times. This process was undertaken using home-built robotic systems.[3, 4] After depositing 13 bilayers of PEI/VMT, the solutions were replaced with SiO_2 and CNCs for another 40

bilayers, as shown in Fig. 1a. This deposition process was carried out until the required number of high (A) and low (B) RI layers were obtained. For simplification, a Bragg stack film with 7 A layers and 6 B layers will be presented as "$(AB)_6A$" in the following sections.

3. Film Characterization

Assembly thicknesses and refractive indices of the PEI/VMT and Si/CNCs bilayer films were measured every bilayer using a PHE-101 Discrete Wavelength Ellipsometer (Microphotonics, Allentown, PA) in absorbance mode, using a 632.8 nm laser at an incidence angle of 65°. Cross-sections of the assemblies were prepared by embedding the film in Epofix resin (EMS, Hatfield, PA) overnight, followed by cutting with an Ultra 45º diamond knife (Diatome, Hatfield, PA). Sections were then imaged with a Tecnai F20 Transmission Electron Microscope (TEM) (FEI, Hillsboro, OR), operated at 200 kV. Cross-sections were also examined with a Nova 600 Dual Beam Scanning Electron Microscope (SEM) (FEI, Hillsboro, OR). The *C. rajah* samples were prepared for TEM using the method outlined by Vukusic et al.[5] The optical properties of the fabricated systems were predicted by modeling combinations of layer thicknesses and refractive indices, obtained from growth profiles, using optical transfer matrices calculated in MATLAB®. Layer thicknesses with associated refractive indices were derived from growth profiles and model data. This analysis determined the deposition cycles of the LbL assembly process, which in this case were 13 bilayers for the A layers and 40 bilayers for the B layers. Optical characteristics of the assembled films were measured using angle-resolved spectrophotometry (ARS).

References

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