Nanocomposites: Layer-by-Layer Assembly of Cellulose Nanocrystals

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Summary

Cellulose nanocrystals are promising as a new class of reinforcing material for the preparation of nanostructured composites. We report here preparation of cellulose nanocrystals multilayer composite with poly(diallyldimethylammonium chloride) using layer-by-layer assembly technique. The LBL assembly was characterized with UV-vis absorbance and ellipsometry. Average thickness of a single bilayer was found to be 11 nm. AFM and SEM characterization revealed uniform coverage and densely packed cellulose crystal surface.

Introduction

Preparation of high performance nanostructured composites has received increasing interest in the recent years. Carbon nanotubes (CNTs), in particular, have received wide attention thanks to their low density, as well as excellent mechanical and electrical properties.[1-12] However, utilization of this material for the preparation of hybrid composites is problematic due to the difficulty of generating stable dispersions, because of their highly hydrophobic surface.[13-17] In addition, for the purpose of large scale production, CNTs are prohibitively expensive, and until cheaper preparation techniques will be developed, it is unlikely that they will find utilization in large scale manufacturing besides some niche high value–added applications.

An alternative may be found in natural and renewable materials. Nanoparticles of natural and inexpensive materials such as clays have received substantial interest as reinforcing fillers for a variety of applications, e.g. thermoplastic polymers, ceramic fibers, or molding composites.[18-21] Another natural nanomaterial, the cellulose nanocrystals (CellNs), is also gaining momentum recently due to the combination of its natural and renewable origins as well as equally impressive mechanical properties when compared to CNTs: bending strength of ~10 GPa and E ~150 GPa,[22, 23] which are only about 10x smaller then those of Single-Walled CNTs (tensile strength predicted to be as high as ~300 GPa at E of ~1 TPa[1, 5], and bending strength of 63 GPa[1]).

CellNs are inherently a low cost material which is available from a variety of natural sources. In the past decade, several reports detailing preparation of suspensions of the nanocrystals from sources such as: cotton,[24] tunicate,[25, 26] algae,[27, 28] bacteria,[29, 30] and wood[24, 31, 32] have been presented. Depending on the source, CellNs are also available in a wide variety of aspect ratios, e.g. ~200 nm long and 5 nm in lateral dimension[24] and up to several microns long and 15nm in lateral dimension[25, 26] from cotton and tunicate respectively. As compared to other inorganic reinforcing fillers, CellNs have additional advantages, including positive ecological: low energy consumption, ease of recycling by combustion, high sound attenuation, and comparatively easy processability due to their nonabrasive nature, which allows high filling levels, in turn resulting in significant cost savings.[33] All of this makes CellNs an attractive nanomaterial for the preparation of low cost, light-weight, and high-strength hybrid composites for multitude of applications.

As such, potential applications of these agro-fiber based composites are currently being researched for automotive, railways, aircraft, irrigation systems, furniture industries, and sports and leisure items.[34-38] Novel applications of CellNs in diverse range of fields were presented recently[39], from iridescent pigments to biomolecular NMR studies. In the nanocomposite field, CellNs have already found applications as solidified liquid crystals for optical applications, e.g. security paper[40, 41], or in the use of whiskers as mechanical reinforcing agents for low-thickness polymer electrolytes for lithium batteries applications[42-46]. From the purely mechanical point of view, recent work has also shown preparation of composites from micro fibrillated cellulose possessing bending strength as high as 370 MPa and E up to 19 GPa[47] and CellNs in combination with silk fibroin resulted in a composite with tensile strength (σ) as high as 160 MPa and E approaching 12 GPa[48].

Clearly, these results in mechanical reinforcement are far from the values that are expected given the properties of CellNs. The problem once again arises from the poor matrix connectivity of the material with the host polymer similarly to CNTs. The problem may be dealt with by immobilizing the reinforcing agent inside of the polymer matrix. In the field of preparation of thin film composites, layer-by-layer (LBL) assembly technique has been shown to provide one of the most promising tools for immobilization of the CNTs as well as obtaining hybrids with high loading of the material. With this technique, we have presented recently preparation of composites from both single- and multi walled carbon nanotubes with tensile strength, σ, reaching as high as 250 MPa (in some cases σ reaching 325 MPa) and *E* as high as 5 GPa.[49-51] LBL assembly allows also for nanoscale organization of the material and using clay nanosheets together with a polycation we have recently reported assembly of a biomimetic nanocomposite with σ = 110 MPa, *E* reaching 13 GPa, and with inorganic material loading up to 85%.[52]

Having these results in mind we have attempted LBL assembly of the CellNs in order to generate even stronger composites in perspective. Although initial reports about preparation of the CellNs multilayers with poly(allyl amine) have been presented recently in the form of a conference presentation[53], here, we report for first time the LBL assembly of nanostructured composite from CellNs and poly(dimethyldiallylamonium chloride) (PDDA) as a first stage in an effort of preparing high strength, low-cost and light-weight thin-films. The sequential deposition of the CellNs with LBL technique opens a new route for nanoscale organization of the material which may potentially lead to other, new developments.

Experimental Part

Materials.

The polymer, poly(diallyldimethylammonium chloride) (PDDA) with molecular weight of MW ~100,000 was purchased from Sigma-Aldrich (St. Louis, MO) and used as received (20 wt% solution) without further purification. Prior to use in the experiments, the stock polymer solution was diluted to 0.5 wt% with 18 MΩ, de-ionized under vigorous stirring for 2 hours. Whatman No.1 filter paper and microscope glass slides were both obtained from Fisher Scientific (Hampton, NH). Hydrogen peroxide and concentrated sulfuric acid used in the piranha solution were both purchased from Sigma-Aldrich.

Cellulose Nanocrystals Preparation.

Cellulose nanocrystals were prepared by sulfuric acid hydrolysis of Whatman No. 1 filter paper powder (98% cotton) as described previously.[24] Briefly, 5g of the ground paper was mixed with 100mL of 64% w/v sulfuric acid and stirred at 45 °C for 1 h. The acid solution was subsequently removed by multiple centrifugation, decantation of the supernatant, and redispersion steps. Purified material was finally redissolved in 100 mL of deionized water and stored in the refrigerator until further use. Prior to use in experiments, suspension with the crystals were redispersed by brief ultra-sonic treatment of the solution with an ultrasonic processor (Cole-Parmer) in order to break up any of the aggregated material.[24]

Layer-by-Layer Assembly.

The microscope glass slides used in LBL assembly were cleaned by boiling in piranha solution (3:1 H_2SO_4:H_2O_2) for 1 hour, followed by thorough rinsing with de-ionized water prior to use. Cleaned glass slides were then sequentially immersed into: 1) 0.5 wt% PDDA solution for 10 min, 2) DI water for 2 minutes in order to rinse any weakly adsorbed material, 3) cellulose nanocrystals solution for 10 min, and 4) DI water for 2 minutes to rinse away any weakly adsorbed CellNs. The entire cycle was then repeated up to ten times for the purpose of the present study although the deposition can be repeated indefinitely. The pH of the rinsing water after CellNs deposition was adjusted to pH = 2-3, in the range of CellNs solution pH, because it showed more uniform growth of the multilayer. After every rinsing step, glass slides were thoroughly dried with compressed air stream before proceeding to the next deposition.

Instrumental Analysis.

Scanning electron microscopy (SEM) images were taken with a FEI Nova Nanolab Dualbeam FIB. SEM sample consisted of a single PDDA/CellNs bilayer which was deposited on a piece of a piranha cleaned silicon wafer following the same procedure as with glass slides. Prior to taking images, sample was coated with a thin layer of gold using a vacuum gold ion sputterer to avoid the charging effect on the sample with the electron beam.

Atomic force microscopy (AFM) imaging was performed in air with a Nanoscope III (Digital Instruments/Veeco Metrology Group) operated in tapping mode using silicon/nitride tips. The sample was prepared in the same manner as for SEM analysis except no gold coating was required.

UV-vis spectroscopy was performed with an 8453 UV-Vis Chem Station spectrophotometer produced by Agilent Technologies. The measurements were obtained by acquiring the absorbance spectrum for a sample deposited on a clean glass slide from 200 nm to 1000 nm after each deposition of a material and comparing the spectrum to that of a pure glass slide. For the purpose of spectrum acquisition, the glass slide was placed directly in the path of light between the light source and the detector.

Ellipsometry measurements were obtained using a BASE-160 Spectroscopic Ellipsometer produced by J. A. Woollam Co., Inc.. The samples used for ellipsometry were similar to those used for SEM and AFM. In particular, layers were deposited on the silicon wafer in the same manner as on glass slides and a scan was obtained after every CellNs layer up to 10 bilayers. The refractive index of the multilayer was determined from a thick sample. This value was then used for the thickness calculation of thin layers. The instrument was calibrated to the standard silicon wafer with a thin layer of silicon dioxide and the overall thickness on the wafer was then fitted using a Cauchy's model.

Results and Discussion

For the purpose of preparation of the hybrid composite we have chosen to work with PDDA since it has received wide attention in the LBL community. PDDA is widely available and its polymer chains contain high density of positive charges per unit length which renders preparation of the multilayers easier as opposed to other weakly charged polyelectrolytes. Sulfuric acid hydrolysis of cotton fibers results in partial conversion of the hydroxyl groups to sulfates, thus imparting negative charges to the nanocrystals and requiring positively charged partner for the assembly. Gray et. al. has also reported a study of adhesion forces on the surface of the CellNs/PDDA samples, which gave a suggestion that assembly with PDDA polymer should be feasible.[54]

In a typical assembly, we have used 10 min adsorption intervals since we have found this to be adequate in many other systems we have prepared previously. To monitor proper assembly, we have used the classical approach and measured UV-vis absorbance spectrum after each deposited bilayer on a glass slide. (Figure 1A). When absorbance at 360nm wavelength was plotted as a function of a bilayer number the graph gave nearly straight regression, indicating uniform assembly and distribution of CellNs in each bilayer. (Figure 1A) The absorbance of the composite reached nearly 0.35 OD after deposition of 10 bilayers, indicating high loading of the CellNs and rapid LBL deposition, which can be contrasted with quite slow deposition of SWNTs due to small surface charge.

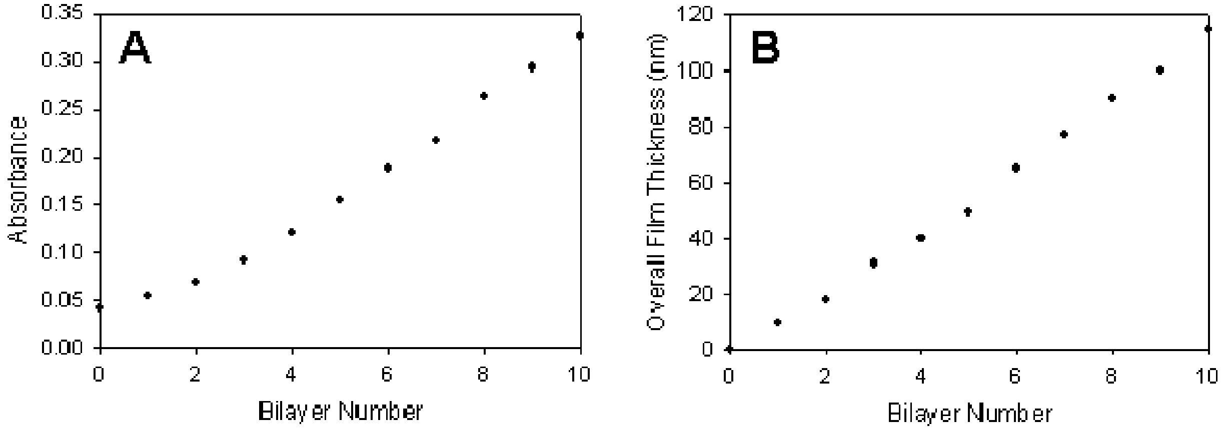

Figure 1. Evolution of a growing composite determined using A) UV-vis absorbance at 360 nm and B) with an ellipsometer after each deposition of cellulose nanocrystals

We have also characterized the thickness of each individual bilayer in the composite using ellipsometry. We have found that an individual bilayer is 11 nm thick and this thickness was consistent for every additional bilayer added to the composite. A plot of the thickness data obtained from ellipsometry once again shows, as expected, a straight line. (Figure 1B) This result is in good agreement with the UV-vis data collected.

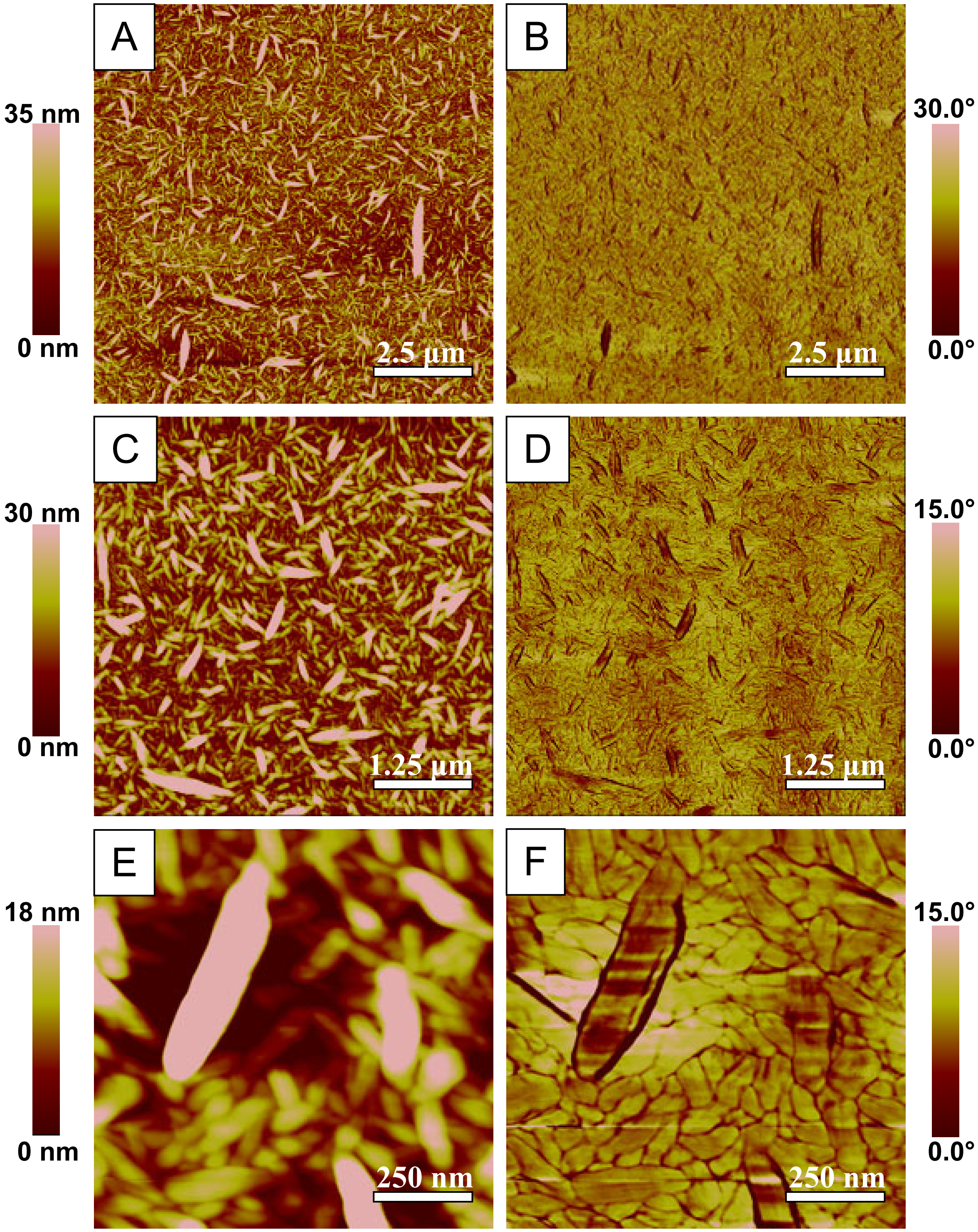

Figure 2. Tapping mode Atomic Force Microscopy image of surface topography for a single PDDA/CellNs bilayer on silicon substrate. 2A and 2B topography and phase images of 10 µm * 10 µm area; 2C and 2D topography and phase images of 5 µm * 5 µm area; 2E and 2F topography and phase images of 1 µm * 1 µm area.

Surface morphology and topology of LBL layers of CellNs was characterized by atomic force microscopy (AFM) as well as scanning electron microscopy (SEM). Following previously reported suggestions we have obtained AFM images while operating in tapping mode, since CellNs have been found to be easily adsorbed on the tip of the probe operating in the contact mode when PDDA is present.[54] Characterization of a single bilayer adsorbed on a silicon wafer revealed very high density and uniform coverage. (Figure 2) In our experience with CNTs assembly, we have not previously observed such high density of coverage with a single bilayer. SEM characterization confirmed high uniformity and dense packing obtained from AFM analysis (Figure 3).

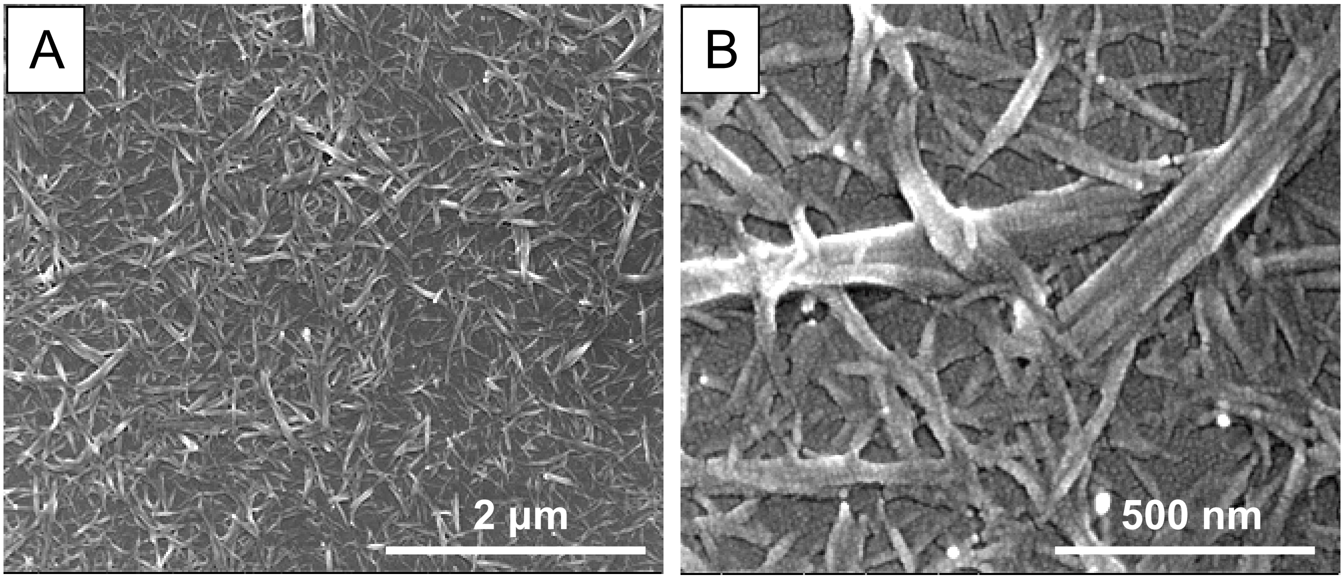

Figure 3. Scanning Electron Microscopy images of a single PDDA/CellNs bilayer on a silicon substrate at 50k (3A) and 200k (3B) magnifications.

CellNs obtained from cotton have been reported to be 5 nm in diameter and 100-300 nm long.[24] Both SEM and AFM are in agreement with these reports. SEM and AFM also show larger crystals which following a closer look (Figures 3C and 3D) clearly show that these are aggregates of CellNs resulting from incomplete digestion of cotton. To avoid these larger aggregates, further purification may be applied. The network morphology of the films is very encouraging structural feature for the creation of ultrastrong materials provided that methods of efficient load transfer and debundling of CellNs are found. These problems are identical to those seen for CNT composites, although approaches to their solutions can be drastically different due to substantially more chemically active structure of CellN backbone.

In conclusion, we have presented here initial results from successful LBL assembly of cellulose nanocrystals and PDDA polycation in an effort of generating a new class of multilayered composites. In the preliminary study, characterization of the multilayer structure revealed tightly packed CellNs layers with high loading of the nanocrystals. Formation of a uniform layer can potentially allow for direct assembly of the nanocrystals with other nanocolloids without the need for polymeric interlayer which will be exploited in the future work. Given their natural origins, CellNs have wide potential for applications in biomedical community as well.

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