Formation of cellulose-based electrostatic layer-by-layer films in a magnetic field

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Abstract

Cellulose has been shown to demonstrate negative diamagnetic anisotropy, and cellulose nanocrystals dispersed in water form a stable chiral nematic liquid crystal phase above a critical concentration. We review some consequences of these two observations when the chiral nematic phase is placed in a magnetic field. Of interest was the possibility of making a layer-by-layer polyelectrolyte film, where the cellulose nanocrystal component was oriented by an applied magnetic field. Preliminary experiments indicated that orientation of the nanocrystal layer could be achieved, but the process was slow.

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1. Introduction

Cellulose is the main structural component of green plants, and as the most abundant material in the biosphere, its properties are of interest as a source of biodegradable and renewable materials. Here, we review interactions of cellulose in magnetic fields, and present preliminary results relevant to the preparation of layer-by-layer films containing cellulose in a magnetic field.

Sugiyama and co-workers [7] examined the diamagnetic anisotropy of native cellulose I crystals dispersed in dilute aqueous suspensions by magnetic birefringence measurements using magnetic fields up to 19T. Under this strong field, the rod-like cellulose crystallites became oriented with their long axes perpendicular to the field direction. Cellulose I nanocrystals form ordered chiral nematic suspensions above a critical concentration [5]. In a magnetic field, these ordered suspensions orient with their chiral nematic axis parallel to the field direction, so that the long axis of the nanocrystals is perpendicular to the magnetic field [6]. Unlike chiral nematic phases composed of species with positive diamagnetic anisotropy, which untwist in a magnetic field, the ordered cellulose nanocrystal phase retains its chiral nematic structure, and simply reorients to give a more uniform planar texture [4]. This reorientation may be observed as an induced circular dichroism for a dye oriented by the ordered phase [1] or in solid films cast from such phases [2]. Recently, Kimura et al. [3] showed that chiral nematic cellulose nanocrystal suspensions could be untwisted by applying a slowly rotating (10 rpm) 10 T magnetic field. Thus magnetic fields are useful, both for reorienting the chiral nematic director to give monodomain samples, and also for untwisting the phase to give a nematic arrangement of the nanocrystals.

Suspensions of cellulose nanocrystals are often stabilized by negative surface charges from carboxyl or sulphate ester groups on their surface. This raises the possibility of using the nanocrystals as the anionic component in electrostatically adsorbed layer-by-layer self-assembled bilayers and multilayers, in combination with cationic polymers. In order to optimize the order of such layered structures, it may be advantageous to assemble them in a strong magnetic field. In this note, we report results of a preliminary experiment, where a layer of cellulose nanocrystals was adsorbed onto a poly(allyl)amine hydrochloride (PAH) coated silicon surface in a magnetic field.

2. Experimental

Electrostatic layer-by-layer self-assembled films of nanocrystalline cellulose and PAH were prepared by conventional solution dipping. The nanocrystalline cellulose was obtained by acid hydrolysis of cotton fibers resulting in a stable colloidal
A suspension of rod-shaped crystals (~100–200 nm long by 5–10 nm wide). The suspension concentration was 9 wt% cellulose (acid form), well into the ordered phase region. PAH (MW = 60,000 g/mol) was obtained from Polysciences (Warrington, PA) and used as received. The multilayer films were assembled on polished silicon wafers from WaferNet, Inc. The silicon wafers were cut to the desired dimensions and cleaned in a concentrated chromium(III) oxide/sulfuric acid bath for 24 h, followed by continuous rinsing with purified water. The anionic surface of the silicon was rendered cationic by adsorption of PAH immediately after substrate cleaning. The dipping procedure included a 25 min immersion of the wafer in a 10^{-2} M PAH bath, followed by three consecutive rinse steps. This coated substrate was then introduced into a chiral nematic suspension of cellulose nanocrystals in the 7 T magnetic field of a solid state NMR spectrometer (see Fig. 1).

3. Results and discussion

When the PAH coated silicon wafer was immersed vertically in a 9% nanocrystal suspension for 30 min, removed, rinsed and dried (in a vertical position), examination of the film surface by AFM showed no orientation of the nanocrystals (Fig. 2(a)). This is perhaps unsurprising; although the magnetic field is known to align the chiral nematic director along the field direction, the nanocrystals remain in a chiral nematic structure, where all nanocrystals are oriented perpendicularly to the field in the x–y plane, but only a few are oriented in the plane of the film (along the y-direction); most are oriented at some angle to the plane of the substrate, and must rotate out of the chiral nematic structure if they are to adsorb flat on the substrate (normally, the chiral nematic phase would rearrange to align the chiral nematic axis perpendicular to the surface, but this is opposed by the magnetic field). The orientation is shown schematically in Fig. 3.

Unexpectedly, by leaving the substrate in contact with the suspension in the magnetic field for a long-time (24 h), a substantial degree of orientation was observed by AFM (Fig. 2(b)). The orientation direction shown in Fig. 2(b) corresponds to the y-direction in Figs. 1 and 3. There may be several reasons for the long-time required for orientation. First, there is a twist elastic energy barrier to the reorientation of those nanocrystals that are not oriented parallel to the y-axis, if they are to adsorb flat onto the substrate (see Fig. 3). If this reorientation is inhibited, and the electrostatic attraction causes adsorption of the nanocrystals without reorientation, then it is not surprising that the initial nanocrystal orientation appears random (Fig. 2(a)). However, the magnetic field will continue to exert a torque on the nanocrystals to orient along the y-direction. This reorientation may be achieved by some

![Fig. 1](image1.png)

Fig. 1. Experimental set-up for adsorption of magnetically aligned nanocrystalline cellulose. The magnetic field propagates along the z-axis (as defined in the figure), which causes the crystals to align in solution perpendicular to B (x–y plane). The substrate is dipped in the y–z plane leading to crystal alignment along the y-direction.

![Fig. 2](image2.png)

Fig. 2. Tapping mode AFM height images (5 μm × 5 μm) of PAH and cellulose nanocrystals adsorbed on a silicon wafer. Films were dipped in the 7 T magnetic field for (a) (1/2) h and (b) 24 h. The arrow in (b) indicates the alignment direction, which corresponds to the y-direction in Figs. 1 and 3.
relatively slow mechanism involving adsorption/desorption or surface migration. Alternatively, following the initial random orientation, there may be a subsequent slow buildup of magnetically oriented material. Note that the twist elastic barrier will increase with concentration, as the chiral nematic pitch decreases, and the concentrated suspensions become more tightly twisted. This may explain why no orientation was observed for a suspension sample at a high cellulose concentration (16 wt% cellulose, sodium form).

4. Conclusions

Preliminary experiments relevant to layer-by-layer self-assembly of oriented cellulose nanocrystals were performed in a 7 T magnetic field. Orientation of the deposited nanocrystals was observed, but only after long exposure to the field.

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