Cellulose Nanocrystal Electro-optic Devices

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Overview

We present here a new, nano-based technology which offers great potential in the field of electronics displays and light modulation.

Current knowledge

The electro-optic effect is the change in the response of a material to light when that material is subjected to an electric field. A large number of applications in everyday life depend on the electro-optic effect. Some of these are: Liquid crystal displays (LCDs) (e.g. digital wristwatches, computer monitors, TV's, etc.), Kerr cells, Pockel cells, Q-switches for lasers, spatial light modulators, optical shutters and variable density filters, and a host of other applications.

The electro-optic effect can arise from many different mechanisms, however, our interest here is on the alignment of anisotropic materials in an electric field. This effect falls under the category of transient electric birefringence (TEB). This method of field induced alignment is based on the interaction between the polarizability of a molecule and an electric field.[2-4] For an anisotropic nanometer-sized object, this interaction will result in the axis corresponding to the largest polarizability rotating to become parallel to the external field. For example, a rod shaped object will align its long symmetry axis parallel to the external field, while a sheet shaped object will align its surface parallel to the field.[5] The degree of alignment is determined by the anisotropy in polarizability and the strength of the electric field. In essence, the rotational force of the electrostatic interaction is opposed by the free rotational diffusion, i. e., Brownian motion, of the object.

Gap in the knowledge base and why this is important

Current optical and display technology is limited by cost, response time, power requirements and various efficiencies, including light transmission. While the TEB of nanoparticles is well documented, we are unaware of any applications based on this effect, until now.

Overall objective for this project to fill the gap above

We have observed the TEB effect in cellulose nanocrystal (CNXL) dispersions in both water and an organic solvent (dimethyl formamide) (Fig. 1). The excellent properties which resulted offer the potential to develop a variety of devices based on this effect. These include: Display technology superior to current TFT-LCD displays; variable density optical filters; light valves. **We intend to develop an electronically controllable variable waveplate, similar to liquid crystal technology, but operating on an entirely different mechanism. This may lead to novel and as yet unknown applications for this new technology.**

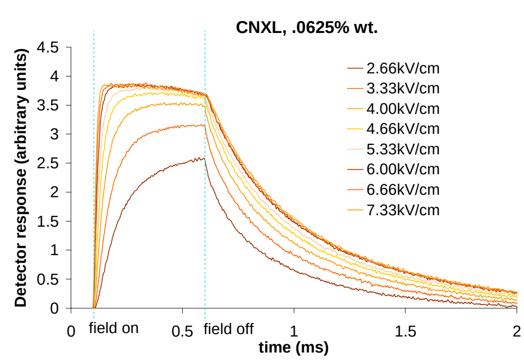

Figure 1. Birefringence of a 0.06% CNXL aqueous dispersion at various field strengths.

Background on CNXLs

CNXLs are derived from nature. Their exact shape can vary from a ribbon to a rectangular long, thin rod depending upon the species from which they are derived. CNXLs have a hydrophilic surface. The cellulose crystal is one of the strongest and stiffest of organic molecules with a modulus of 145 GPa[6] and a strength estimated at 7500 MPa.[7] The surface area of CNXLs has been measured at ~ 250 m^2/g (for CNXLs from the bacteria A. Xylinum).[8] In addition, cellulose is imminently modifiable via a host of well known chemical reactions.[9] Few nanoparticles offer the versatility in terms of ease of preparation and chemical modification that is present in cellulose. For CNXLs obtained from wood or cotton, typical sizes range from 4 to 10 nm in width and 50- 200 nm in length (Fig. 2)

Background on TEB

The theoretical treatment of field induced alignment of nanoparticles in dispersions has been documented in detail.[2-4] However, the application of this approach has not been extensively explored. AC electric fields have been used to align carbon nanotubes, and the higher is the oscillation frequency, the higher is the degree of alignment.[10] The application of AC induced alignment, unfortunately, is limited in that some nanometer sized objects are charged, which causes heating and limits the size of the applicable AC field. Pulsed field induced alignment has been used to measure the size, shape, and flexibility of many microscopic biological objects and synthetic polymers.[11] An advantage of a pulsed field is that its dependence on the conductivity of the solution medium is much less stringent than that of an AC field.[12]

In a weak DC electric field, the ultimate degree of alignment is given by:

$$< P_2 >_{\max} = \frac{\delta\alpha\ E^2}{5\ k_B\ T} \ , \qquad (1)$$

where T is the temperature and k_B is the Boltzmann constant. We can estimate the value of $\delta\alpha$ based on the polarizability volume of the particle. For a long, thin cylinder of volume 400 nm^3 in a 5 kV/cm field at room temperature, the alignment is $<P_2>_{max} \sim 0.1$.

The time profile of the alignment effect is an exponential function:

$$< P_2(t) > \ = \ < P_2 >_{\max} (1 - e^{-\Lambda\, t}), \qquad (2)$$

where Λ is determined by the diffusion constant D_r (which is in turn dependent upon a number of variables) and the field strength E. It is possible, though not straightforward, to estimate the diffusion constant for rod-shaped objects. On the other hand, we have succeeded in measuring the time profile experimentally using a pulsed electric field (Figs. 1 and 3).

Background on display technology

The TEB effect finds practical application in liquid crystal (LC) displays. Here a LC polymer moves in response to an electric field. Typically in display devices (Fig. 2), liquid crystal materials are assembled as 5 μm films. A "rubbing" process orders them into a twisted nematic structure which typically rotates the incoming light through 90° (This rubbing process is unnecessary using CNXLs). A set of crossed polarizers are placed outside the liquid crystal medium, thus the rotation due to the LC results in light transmission through the exit polarizer. This is called a "normally white" display. An electric field along the line of sight aligns the LC molecules, "untwisting" them, and removing the change in the polarization direction of the light. Consequently, no light passes through the exit polarizer while the electric field is applied. A circuit is lithographed on the thin film transistor (TFT) substrate which applies the electric field and provides a capacitance

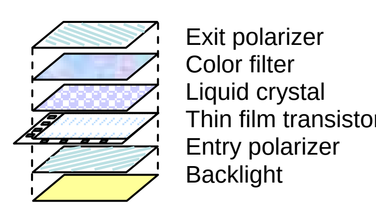

Figure 2. Schematic of liquid crystal display element.[1]

which maintains the state of the LC during the frame time (time to refresh the display screen). A common electrode composed of indium tin oxide (ITO) is applied to the color filter to complete the circuit.

Preliminary experimental results

The time constant for the rise of the birefringence is a function of the square of the applied electric field. The rise time, i.e. the time required for the birefringence to reach 90% of its value at full alignment, i.e. $<P_2>_{max}$, for a 1.6% CNXL dispersion at a field strength of 0.12 V/μm was 32 μs. Furthermore, the transmittance of the incident light was 77%. This compares with typical rise times in commercial LC devices of 2-4 ms (utilizing Overdrive technology)[13] and a transmission efficiency of ~40%.[14] Further, typical field strengths for commercial LCDs are ~ 1 V/μm, roughly an order of magnitude higher than the CNXL system.[1]

Alignment induced by a pulsed electric field has long been known from measurements of TEB.[15] The degree of alignment depends on the concentration, the charge density on the particle, the size of the particle, and the viscosity of the solution.[15] TEB has been, and still remains, one of the most powerful methods for characterizing the size and size distribution of nanometer to micrometer sized particles in solutions.[2,16]

The degree of alignment of nanoparticles in the electric field can be measured from the difference in refractive indexes parallel ($n_{//}$) or perpendicular ($n_{\perp}$) to the electric field.[9] This method of detection has been utilized since it was introduced in the 1950s when pulsed electric fields were first used for alignment.[15]

A special case of TEB is the Kerr effect, which is technically anything that obeys the Kerr equation, which is:

$$\Delta n = K \lambda E^2 \tag{3}$$

where n = refractive index, K = Kerr constant, λ = wavelength of light, and E = electric field strength. Our CNXL data follow this equation (Fig. 3). All substances exhibit a Kerr effect, however, the extent of the effect varies considerably. If the applied field is from a laser, it is called the optical Kerr effect. In addition, the Kerr effect can be caused by anisotropy induced in the electron clouds of molecules. By this mechanism it is typically very fast, giving rise to a change in refractive index in the picosecond range. The effect we see, while coincidentally obeying the same equation, is much slower than this and thus arises from the rotation of the nanoparticles in the applied field.

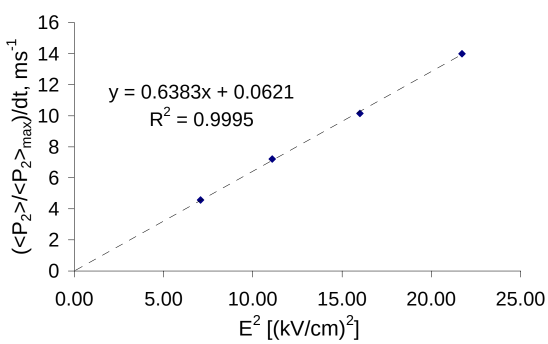

Figure 3. Kerr plot of the birefringence rise time in a 0.016% aqueous CNXL dispersion.

Oscillatory behavior

We have also observed that the CNXL system exhibits a complex oscillating TEB effect that depends upon the concentration, electric field strength, and path length of the optical cell (Fig. 4). These oscillations can be explained by the fact that cellulose is an extremely birefringent material. The difference in birefringence between the a and c planes in a cellulose film is $\Delta n = 1.45 \times 10^{-2}$.[17] The CNXLs act as birefrengent retardation waveplates. The phase shift is given by:[18]

$$\Gamma = \frac{2\pi L \Delta n}{\lambda} \tag{4}$$

Where Γ = the phase shift and λ = wavelength of the light and L is the pathlength through the waveplate. As the CNXLs rotate into the direction of the field, Γ rotates through π/2 more than once due to the long pathlength of our current cell (~1 cm). At each π/2 value, the light is parallel to or crossed with the exit polarizer, thus the light output oscillates. The oscillations can thus be controlled by controlling the CNXL concentration, path length, and/or electric field in the system.

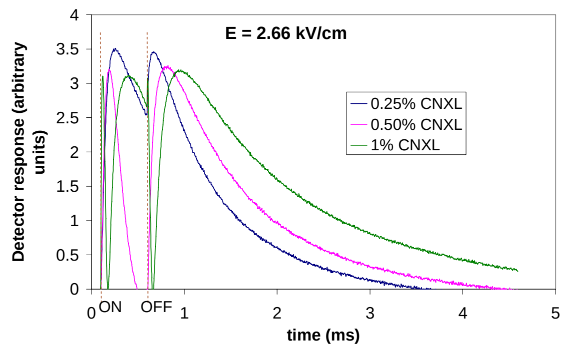

Figure 4. Oscillations in birefringence for various CNXL concentrations at 2.9 kV/cm

Description of proposed work and rationale that this approach will work

The observation of this effect is relatively new. Thus, a great deal of work is needed to develop both the experimental data set and theoretical understanding of this system. Specifically:

1. Optics: The current research optical system will be modified to accommodate a variety of optical cell configurations to test and evaluate the performance with respect to pathlength, temperature, field vs. conductivity of the liquid, i.e. power requirements, and optical efficiencies.
2. Devices: will be constructed on a size scale appropriate for display and other optical technologies.
3. Chemistry: The size and shape of CNXLs can be controlled within limits by selecting the appropriate species as starting material and the processing conditions for obtaining the CNXLs. Thus, we can explore the preparation of various CNXL sizes, shapes, and size distributions. The TEB effect is also dependent on the surface charge on the CNXLs, as well as the type of counterions present. These properties can be readily controlled by surface functionalization and subsequent ion exchange chemistry. In addition, critical knowledge to be developed for the application of CNXL dispersions includes the optimization of colloid dispersion and the stability of the colloidal phase, the evaluation and improvement in thermal stability of CNXLs produced, and the optimization of colloid viscosity and conductivity.
4. Theory: Developing a firm theoretical basis for this effect will not only allow for the precise design of various devices, but will perhaps open the door to exploiting this effect of anisotropic nanoparticles in other areas and utilizing other materials.

Summary

Current TFT-LCD technology is advanced and evolving rapidly. However, we feel that this nanoparticle approach has advantages not offered by liquid crystals, including speed, power and cost. At the same time, we have potential obstacles to overcome, including dispersion stability and the fabrication and durability of liquid-containing devices.

This CNXL electro-optic effect is an unusual characteristic of the natural world and has the potential to advance technology in a number of areas. We intend to see that the phenomenon is thoroughly documented, theoretically understood, professionally published in the peer-reviewed scientific literature, and commercially applied. A provisional patent has been filed on the technology.

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