Published in final edited form as:

Opt Mater Express. 2011 September 1; 1(5): 936–942. doi:10.1364/OME.1.000936.

Linear birefringence magnitude of artificial self-assembled DNA crystals

Anni Lehmuskero^{1,*}, Nina Hakulinen², Hanna Lajunen¹, Jianping Zheng⁴, Ruojie Sha⁴, Benfeng Bai³, Lingling Huang³, Jari Turunen¹, Pasi Vahimaa¹, and Nadrian C. Seeman⁴

¹University of Eastern Finland, Department of Physics and Mathematics, FI-80101 Joensuu, Finland

²University of Eastern Finland, Department of Chemistry, FI-80101 Joensuu, Finland

³Tsinghua University, Department of Precision Instruments, Beijing 100084, China ⁴New York University, Department of Chemistry, New York 10003, USA

Abstract

We determine the linear birefringence magnitude, i.e. the difference between refractive indexes along the extraordinary and ordinary axes, of artificial uniaxial DNA crystals assembled with the so-called DNA tile approach. Based on the ellipsometric measurements, the birefringence magnitude is between 0.001 and 0.0018 in the visible and near infrared range. Besides being of fundamental interest, the optical properties of DNA crystals are crucial in the design of novel photonic nanostructures.

1. Introduction

Humankind has recently reached the ability to build structures with molecular precision. Nucleic acids are used as building blocks to form designed, artificial DNA self-assemblies controlled at the molecular scale [1]. The DNA self-assembly techniques can be used to produce 2D or 3D crystals in which the designed DNA sequence determines the optical properties. Therefore, the optical properties can be tailored and differ from natural materials.

The importance of the DNA techniques is also emphasized by their ability to assemble metallic nanoparticles into a periodic lattices [2–4]. Because of the electric resonances in the particles and due to the small structural dimensions, such nanoparticle structures have the potential to become new types of metamaterials with optical effects also in the visible range [5].

So far, there has been only a small amount of research on the optical properties of DNA related structures [6]. Therefore, in this work we explore the optical properties of artificial 3D DNA crystals, assembled with the so-called DNA tile approach [7]. We measure the changes in the state of polarization of light propagating through the crystals at visible and IR spectral ranges and reveal the birefringence magnitude, the difference between the ordinary and extraordinary refractive indexes.

2. Experimental

2.1. Crystal Growth

Crystals were grown by the hanging-drop technique at room temperature. A crystallization drop (6 μ l) contained 0.25 mg/ml DNA, 50 mM ammonium sulphate, 5 mM magnesium chloride, 25 mM Tris buffer at pH 8.5. The drops were equilibrated against a 0.5 ml reservoir solution containing 1.6 M ammonium sulphate. Crystals appeared after 3–4 days and attained their maximal dimension (usually approximately $100 \times 100 \times 100 \mu\text{m}$) in about one week.

The crystals have a tensegrity triangle with three-fold rotational symmetry, previously designed and described in Ref. [1]. The crystal lattice, shown in Fig. 1, is rhombohedral which belongs into the trigonal crystal system and is therefore uniaxial [8].

2.2. Ellipsometric measurements

In order to conduct optical measurements, the artificial DNA crystals were mounted into thin walled borosilicate capillaries of 0.7 mm diameter. First, a crystal was picked up from the crystallization drop and placed into the capillary using a syringe. Then, the excess mother liquor was removed from around the crystal with a thin strip of filter paper, taking care not to touch the crystal. A small portion of mother liquor was left inside the capillary to prevent the crystal from drying. At the end, both capillary ends were sealed with wax.

The optical measurements were made with variable angle spectroscopic ellipsometer VASE provided by J.A. Woollam co.. The incident beam of approximately 2 mm in diameter was focused onto the crystal with an achromatic lens with a focal length of 3.5 cm. The focal spot was about the same size as the crystal. The focused beam was paraxial to the sample surface, so that only the electric field component parallel to the surface was present. We used linearly polarized light and the transmission mode in the measurements. Light was focused onto the crystal at normal angle of incidence and the polarization azimuth angle of the input beam, indicated by P in Fig. 1, was varied between 10–160 deg in order to measure the polarization dependent properties of the DNA sample. The spectral range was from 380 nm to 1000 nm by steps of 10 nm. Measuring smaller wavelengths was not possible with the same setup due to the UV absorption of the focusing lens. The schematic of the measurement setup and an optical microscope image of the crystal are shown in Fig. 2.

2.3. Definition of the measured parameters

The Jones matrix for an uniaxial anisotropic material is given by [9]

$$\mathbf{J} = \begin{pmatrix} t_{pp} & t_{ps} \\ t_{sp} & t_{ss} \end{pmatrix}, \quad (1)$$

where

$$t_{pp} = t_e \cos^2 \theta + t_o \sin^2 \theta, \quad (2)$$

$$t_{ss} = t_e \sin^2 \theta + t_o \cos^2 \theta \quad (3)$$

and

$$t_{ps}=t_{sp}=(t_e-t_o)\cos\theta\sin\theta. \quad (4)$$

In Eqs. (2)–(4) $t_e = T_e \exp(ikn_e d)$ and $t_o = T_o \exp(ikn_o d)$ are the complex amplitude transmission coefficients for extraordinary and ordinary axes in which d is the thickness of the crystal, k is the wave number in vacuum, and n_e and n_o are the refractive indexes along the extraordinary and ordinary axes. The angle θ is the rotation angle between the ellipsometer coordinate system (p-polarization, s-polarization) and the anisotropic crystal coordinate system (extraordinary axis, ordinary axis).

The ellipsometer uses a polarizer to control the polarization state of the input beam and a rotating polarizer (analyzer) as the output detector. Then, the electric field at the detector is given by the product of the analyzer matrix (the first two matrices in the following equation), sample matrix, polarizer matrix and input beam Jones vector [10]

$$\mathbf{E}_d = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \cos A & \sin A \\ -\sin A & \cos A \end{pmatrix} \mathbf{J} \begin{pmatrix} \cos P & -\sin P \\ \sin P & \cos P \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad (5)$$

where A is the analyzer azimuth angle and P is the polarization azimuth angle of the input beam.

The intensity signal may be calculated by multiplying the electric field E_d with its complex conjugate. The resulting normalized signal is sinusoidal

$$I \propto \alpha \cos(2A) + \beta \sin(2A) + 1, \quad (6)$$

where α and β are the Fourier coefficients of the signal. By inserting Eq. (1) into Eq. (5) and normalizing the resulting intensity we get theoretical expression for α and β in terms of the anisotropic crystal parameters

$$\alpha = \frac{(|t_{pp}|^2 - |t_{sp}|^2)\cos^2 P + (|t_{ps}|^2 - |t_{ss}|^2)\sin^2 P + 2[\Re(t_{pp}t_{ps}^*) - \Re(t_{ss}t_{sp}^*)]\sin P \cos P}{(|t_{pp}|^2 + |t_{sp}|^2)\cos^2 P + (|t_{ss}|^2 + |t_{ps}|^2)\sin^2 P + 2[\Re(t_{pp}t_{ps}^*) + \Re(t_{ss}t_{sp}^*)]\sin P \cos P} \quad (7)$$

and

$$\beta = \frac{2\{\Re(t_{pp}t_{sp}^*)\cos^2 P + \Re(t_{ss}t_{ps}^*)\sin^2 P + [\Re(t_{pp}t_{ss}^*) + \Re(t_{sp}t_{ps}^*)]\sin P \cos P\}}{(|t_{pp}|^2 + |t_{sp}|^2)\cos^2 P + (|t_{ss}|^2 + |t_{ps}|^2)\sin^2 P + 2[\Re(t_{pp}t_{ps}^*) + \Re(t_{ss}t_{sp}^*)]\sin P \cos P}. \quad (8)$$

The actual parameters given by the ellipsometer are ψ and δ . They are related to the Fourier coefficients by

$$\tan\psi = \sqrt{\frac{1+\alpha}{1-\alpha}} |\tan P|, \quad (9)$$

and

$$\cos\delta = \frac{\beta}{1-\alpha^2} \frac{\tan P}{|\tan P|}. \quad (10)$$

The ellipsometric parameters ψ and δ may also be interpreted by

$$\tan\psi e^{i\delta} = \frac{E_p e^{i\varphi_p}}{E_s e^{i\varphi_s}}, \quad (11)$$

where E_p and E_s are the amplitudes of the transmitted p- and s-polarized electric field components and φ_p and φ_s are their phases.

3. Experimental birefringence magnitude

The birefringence magnitude $\Delta n = |n_o - n_e|$, shown in Fig. 3, has been obtained by minimizing the difference between the experimental and modeled α and β for each wavelength separately. The rotation angle of the coordinate systems, θ , was also fitted simultaneously. The experimental Fourier coefficients have been solved from Eqs. (9) and (10) after inserting the measured values of ψ and δ into them. The modeled Fourier coefficients have been calculated by using Eqs. (7) and (8). The thickness of the crystal used in the calculations was 48 μ m. Furthermore, we have assumed that the amplitude transmission coefficients are same in both polarization directions, i.e. $T_e = T_o$. In reality, the polarization-dependent Fresnel reflections at the crystal surfaces may lead to different values for T_e and T_o [8], but in this case the birefringence is so small that this difference is negligible.

As shown in Fig. 3, the birefringence magnitude ranges between 0.001 and 0.0035 for different azimuth angles and for different wavelengths. The differences between azimuth angles should not exist and, therefore, is most probably caused by a small tilt in the crystal orientation from the normal plane of the incident beam or by slanted edge of the crystal which correspond to the case of oblique angle of incidence.

According to Fig. 3 the birefringence is largest at the small wavelengths. This could be explained by the small dimensions of the lattice structure, which was shown in Fig. 1. For smaller structure dimensions the optical effects are expected to shift towards shorter wavelengths. Furthermore, the overall values are smaller than for most of the common uniaxial crystals, such as ice or quartz. This could be explained by the densely packed lattice that produces only small differences in the optical properties for different directions.

The measured and modeled Fourier coefficients, α and β , are shown in Fig. 4. In addition, the experimental and modeled ellipsometric parameters ψ and δ are given in Fig. 5. All the modeled results are calculated by using the birefringence magnitude of 10 deg azimuth in Fig. 3, which is close to the average.

Due to the orthogonality of the ordinary and extraordinary axes of a uniaxial crystal, the Fourier coefficients and the ellipsometric parameters for azimuth angles differing by 90 deg should be the same or form symmetric pairs in case of normal angle of incidence and in-plane anisotropy. The asymmetry in the experimental data pairs (10 deg, 100 deg), (40 deg, 130 deg), and (70 deg, 160 deg) in Figs. 4 and 5(a), and the differences within the same data pairs in Fig. 5(b) could be explained again by the tilt in the angle of incidence.

It is evident from Fig. 3 that the results for 40 deg and 130 deg azimuth angles are noisier than the others. The polarization state of the transmitted beam for 40 deg and 130 deg

azimuth angles remains almost linear (δ in Fig. 5(b) is close to zero), and therefore we may conclude that these directions are close to the ordinary and extraordinary axes of the uniaxial DNA crystal. Because light polarized along 40 deg and 130 deg azimuths is mostly affected only by one of the two principal axis, the data for α , β , ψ , and δ is insensitive to the birefringence magnitude and we may neglect the results for 40 and 130 deg azimuths in Fig. 3. Therefore, the actual values for the birefringence magnitude stay between 0.001 and 0.0018.

The rotation angle of the two coordinate systems, θ , is determined by the direction of the principal axis which is close to 40 deg. The more accurate value, $\theta = 37$ deg, was obtained by choosing the rotation angle that brought the birefringence magnitudes of difference azimuths in Fig. 3 closest together. The thickness of the crystal, $48 \mu\text{m} \pm 10 \mu\text{m}$, was estimated from the optical microscope images.

The error for the birefringence magnitude is mostly dictated by the thickness of the crystal which is directly proportional to the birefringence magnitude. To demonstrate the effect of the thickness, the birefringence magnitude for the 10 deg azimuth angle is calculated in Fig. 6 for the smallest and largest thickness estimates.

4. Conclusions and outlook

We have measured the linear birefringence of artificial self-assembled DNA crystals. The values for the birefringence magnitude for wavelengths of 380–1000 nm are between 0.001 and 0.0018 which makes the crystal weakly birefringent. However, it is good to keep in mind that the polarization effects might be enhanced by adding metallic nanoparticles into the crystal lattice. Such structures could provide a stepping stone to new types of metamaterials. Our current results are expected to be beneficial in the optical modeling and design of such new materials.

Next, it would be interesting to examine the properties of DNA crystals in the UV, where the chirality of the DNA introduces additional polarization effects. Furthermore, the same measurements could be done for DNA-assembled nanoparticle lattices as soon as their fabrication technique produces samples that are large and stable enough for the measurements.

Acknowledgments

This research has been supported by the strategic funding of the University of Eastern Finland and the Finnish Graduate School of Modern Optics and Photonics. B. Bai would like to acknowledge the support by the Academy of Finland (Project No. 128420) and the National Natural Science Foundation of China (Project No. 11004119). The work is also supported by GM-29554 from NIGMS, grants CTS-0608889 from the NSF, and N000140911118 from ONR.

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Fig. 1. Artificial DNA crystal lattice. The rhombohedral unit cell, indicated by the red box, has an edge length of 69.22 Å. The red-colored DNA strands indicate the tensegrity $\triangle$ triangle.

Fig. 2. Setup for the polarization dependent transmission measurements. Incoming polarization state (yellow arrow on the left-hand side) was kept linear while the polarization azimuth angle, P , was varied between 10–160 deg by steps of 30 deg. In the inset, the optical microscope image of an artificial DNA crystal inside a mother liquid drop is shown. The length scale is approximated.

Fig. 3. Birefringence magnitude, Δn , of the DNA crystal for different polarization azimuth angles.

Fig. 4. Measured (solid line) and modeled (dashed line) Fourier coefficients for the detector signal. Colors indicate input beam polarization azimuth angles.

Fig. 5.

Measured (solid line) and modeled (dashed line) ellipsometric parameters ψ and δ . Colors indicate input beam polarization azimuth angles. In case of δ the theoretical results for 10° and 100° follow the same line. The same is valid also for 40° and 130° , and 70° and 160° .

Fig. 6. Birefringence magnitude for 10 deg azimuth in case of minimum (38 μm), estimated (48 μm), and maximum (58 μm) crystal thickness.