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Biopolymer-based material for optical phase conjugation

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We present results of optical phase conjugation experiments in modified DNA (deoxyribonucleic acid) - dye system. The system consisted of a biopolymeric matrix made of DNA blended with cationic surfactant molecule cetyltrimethyl-ammonium chloride (CTMA) and doped with a photochromic dye Disperse Red 1. Results were obtained in a typical degenerate four wave mixing experiment. For sample excitation we used linearly polarized light at a wavelength 514.5 nm, delivered by an argon ion (Ar^+) laser. The phase conjugated signal which emerged from the sample had rise and fall time constants of a few milliseconds with an excellent reversibility.

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1. Introduction

Deoxyribonucleic acid (DNA), with its unique properties derived from its double-helix structure, is a very promising material for photonic applications [1-5]. It has been reported earlier that DNA has excellent optical and electromagnetic properties [6-9] (low optical loss, tunable resistivity, strong enhancement of fluorescence emission, etc.), which suggests potential applications for electro-optic systems, optical memory and light amplification.

In this paper we focus our attention on the process of optical phase conjugation, observed for the first time in a novel photonic system, a complex DNA- cetyltrimethyl-ammonium chloride (CTMA) loaded with a photochromic dye Disperse Red 1. Optical phase conjugation belongs to the group of third order nonlinear processes, observed in a degenerate four-wave mixing experiment (DFWM) [10]. The phenomenon consists in generation of a beam with reversed sign of the spatial part of the wave phase with respect to that of the incident beam. The intensity of the conjugated beam depends on the optical Kerr susceptibility of the medium and intensities of the interacting beams. This gives many possibilities of applications such as compensation of front phase aberrations, light amplification, etc.

2. Sample preparation

For the preparation of the DNA-CTMA complex we used DNA sodium salt, extracted from salmon milt and roe sacs (M_W: 1.3 *10^6, ca. 2000 base pairs), purchased from the Chitose Institute of Technology (CIST) in Japan. The DNA was separated from other constituents, present in salmon milt and roe sacs. The procedure leading to obtaining pure DNA, which includes homogenization, enzyme treatment, protein elimination, carbon treatment, freeze drying and purification, is described in Ref. 6. In order to decrease its molecular mass the water solution was sonicated using a commercial ultrasonic source.

Pure DNA is known to be soluble in water only and exhibits poor temperature stability (degradation at around 90°C). It is also difficult to process into good optical quality thin films. In contrary, it is well known that the complex of DNA – with CTMA is soluble in alcohols and can be processed into very good optical quality thin films by solution casting and spin deposition [8]. We used commercial CTMA surfactant (Aldrich) and followed the procedure described in literature to make the DNA-CTMA complex. The solvents were purchased from Aldrich and used as supplied, without any further purification. The complex is soluble in common organic solvents but insoluble in water.

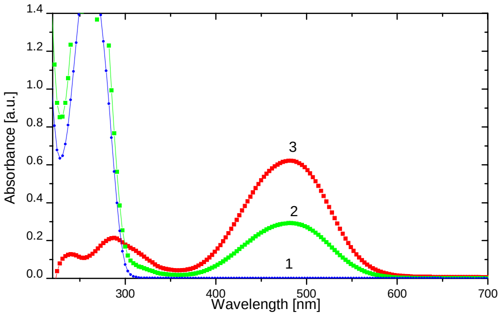

Fig. 1. Absorption spectra of DNA-CTMA (curve 1), DNA-CTMA-DR1(5%) (curve 2) and DR1 in solution (curve 3).

The layers of DNA and DNA-CTMA complex are highly transparent because of a limited π electron conjugation (phenyl rings) (cf. Fig. 1). In order to get a light sensitive material the DNA-CTMA complex was doped, in solution, by the well known photoizomerizing chromophore: 4-(4-Nitrophenylazo)diphenylamine (Disperse Red 1, DR1). The chromophore, purchased from Aldrich, was purified by a double recrystallization, from absolute methanol solution. It was solubilized in butanol and added to the DNA-CTMA solution, also in butanol, in a given proportion in order to obtain the required 5% wt/wt dye concentration.

The thin films were prepared by spin coating, on carefully cleaned glass substrates. The cleaning procedure consisted on washing the substrates in a very clean water bath containing very active detergent and applying ultrasounds. Then substrates were washed several times in deionized water. The last step consisted of 2 hours of drying in a 200°C oven in order to remove any organic matter.

The solution of DNA-CTMA-DR1 was filtered through a 0.2 μm nylon syringe filter prior to spin deposition. We measured a film thickness of 2 μm.

Fig. 1 is a plot of the absorption spectra of DNA-CTMA, DNA-CTMA-DR1 (5% wt/wt) complex and of DR1 in butanol solution.

The UV absorption of nucleobases at around 260 nm is clearly seen in the first two absorption spectra. This strong absorption band corresponds to the π-π^* transition of electrons of the C =C bond of DNA bases. The second absorption band at around 490 nm in DNA-CTMA-DR1 (spectrum 2) is similar to that of pure DR1 (spectrum 3), showing minor solvent influence (solvatochromic effect). We assumed a refractive index of the DNA-CTMA-DR1 complex to be n ≈ 1.53 at λ = 514.5 nm according to Ref. [9].

3. Experimental

The theory of optical phase conjugation is well known and has been described in several papers [10-13]. The electric field

$$\bar{E}^{(3)}(\bar{r},t) = \bar{\varepsilon}A^{(3)}\exp\left[i\left(\bar{k}_3\cdot\bar{r}-\omega t\right)\right] \quad (1)$$

of a plane monochromatic signal wave with polarization denoted by a unit polarization vector $\bar{\varepsilon}$, wave vector $\bar{k}_3$ and angular frequency ω, incident on the sample (cf. Fig. 2), after reflection from a nonlinear optical medium (an ideal phase-conjugate mirror), shows a phase reversal and amplification

$$\bar{E}^{(4)}(\bar{r},t) = \mu\bar{\varepsilon}^{*}A^{(3)}\exp\left[i\left(-\bar{k}_3\cdot\bar{r}-\omega t\right)\right] \quad (2)$$

In equation (2) the coefficient $\mu = A^{(4)*}/A^{(3)}$, denoting the amplitude reflectivity, is given by:

$$\mu = igLA^{(1)}A^{(2)} \quad (3)$$

where $A^{(1)} = \sqrt{4I_1/(\varepsilon_0 nc)}$ and $A^{(2)} = \sqrt{4I_2/(\varepsilon_0 nc)}$ are the amplitudes of the two counterpropagating pumping waves coherent with the signal wave, L is the thickness of the nonlinear medium and g is a coupling constant proportional to the resonance third order nonlinear susceptibility ($g \sim \chi_R^{(3)}(-\omega;\omega,\omega,-\omega)$). In this case the $\chi_R^{(3)}(-\omega;\omega,\omega,-\omega)$ susceptibility describes the ability of the nonlinear optical material to change its refractive index proportionally to the light intensity ($n = n_0 + n_2 \cdot I$) via photochromic effect.

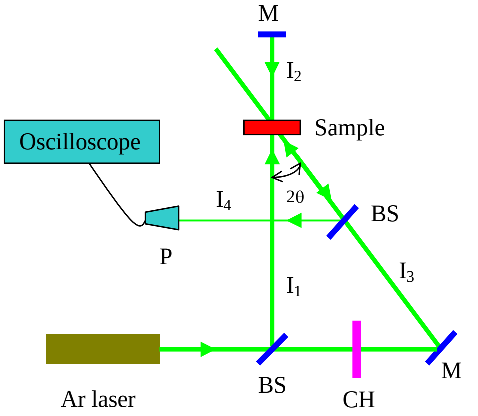

Fig. 2. Optical phase conjugation experimental set-up. BS - beam splitter, CH - chopper, M – mirror, P – fast photodiode.

The degenerate four-wave mixing experimental configuration used for the observation of the phase conjugation process is shown schematically in Fig. 2. Two s-polarized counterpropagating beams - I_1 and I_2 of intensities 1.8 W/cm^2 and 1.3 W/cm^2, respectively and I_3 (s-polarized probe beam), all coming from the Ar$^+$ ion laser (cw, P = 500mW, λ = 514.5 nm, Innova 90, Coherent) were crossing in the sample. The two interfering beams I_1 and I_3, at the angle $2\theta = 33^{\circ}$, generated local changes in refractive index of the medium, consistent with the interference pattern. The pump beam I_2, diffracted on the induced grating towards the direction of the I_3 beam, produces the I_4 beam, conjugated in phase to the probe beam I_3. For the measurements of the dynamics of the growth of the phase conjugate signal I_4, we used a chopper positioned on I_3 beam and high-speed photodetector (Thorlabs) connected to a digital oscilloscope (Tektronix, TDS 220).

In Fig. 3 the evolution of the phase-conjugate signal, measured under chopped cw laser illumination, is presented. We observed that the optical signal which emerges from the sample had rise and fall time constants of a few milliseconds ($\tau \approx 2$ ms). These time constants were obtained by fitting the growth of the conjugated signal using a single exponential growth function.

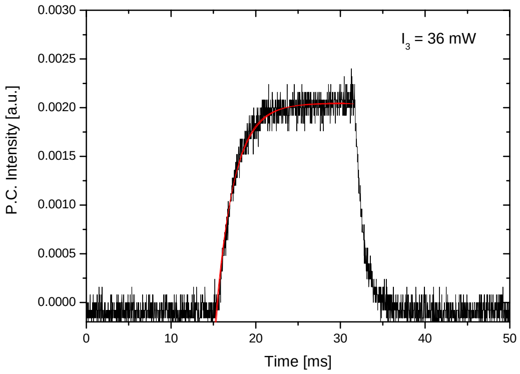

Fig. 3. Phase conjugated signal evolution measured under chopped cw illumination. Time constant of the signal formation $\tau \approx 2ms$.

The optical phase conjugation process with DR1 molecule was observed in different types of matrix like poly(methyl methacrylate) [14, 15] or polystyrene [16] but in all of the cases the time of grating formation was slower than that measured in DNA-CTMA-DR1. Very fast diffraction grating generation is also not the only advantage of this material for use in the processing of optical information. Fig. 4 shows a plot of the sequence of the phase conjugation signals with the probe I_3 beam, chopped at frequency of 10 Hz. In the 500 ms time period the phase conjugate signals were recorded with an excellent reversibility. In addition, no residual light diffraction was observed after each light closure in optical phase conjugation experiment evidencing the lack of any permanent grating in the material. The same was true for longer time exposures (up to few hours).

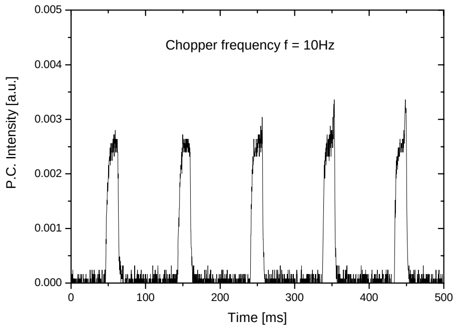

Fig. 4. Sequence of the phase conjugation signal recording and erasing. Reference I_3 beam was chopped with frequency 10 Hz. Intensity of the I_3 beam was 4 W/cm^2.

We have also checked the influence of the probe beam I_3 intensity on the formation time of phase conjugation signal. The results are presented in Fig. 5.

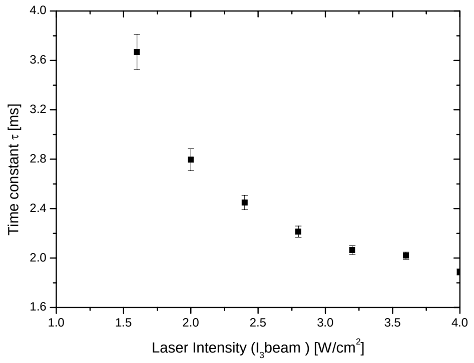

Fig. 5. Phase conjugation signal formation time constant τ *in function of intensity of the I_3 laser beam.*

For low probe beam I_3 intensity, the time constant of the I_4 signal growth was around $\tau \approx 3.7$ ms and diminished with the increase of I_3 , reaching a value $\tau \approx 1.8$ ms for I_3 = 4W/cm^2, being the highest possible intensity in our experimental set-up.

The optical phase conjugation reflectivity, defined as:

$$R_c = \frac{I_4}{I_3} \cdot 100\% \tag{4}$$

was in the range of 0.001% . Such a low reflectivity is partially due to the low thickness (L =2 μm) of the sample, as R_c scales quadratically with L and partially due to the magnitude of the coupling constant g which we estimated to be $g = 3.25 \cdot 10^{-7}$ [m/V^2]. Using the equation relating g with $\chi^{(3)}$ [17]:

$$g = -\frac{12\pi\, i\omega}{nc}\chi^{(3)} \tag{5}$$

we get $\chi^{(3)} = 1.103 \cdot 10^{-15}$ [m/V]^2 ($\chi^{(3)} = 7.8 \cdot 10^{-8}$ [esu]) what is in agreement with the results presented by Rangel-Rojo et. al. [18]. The value of $\chi^{(3)}$ obviously depends on the dye content in the DNA-CTMA complex.

4. Discussion

The microscopic mechanism of the dynamic diffraction grating formation in DNA:CTMA-DR1 system is not yet well understood. There are three possible mechanisms responsible for its formation (i) dye reorientation due to multiple *trans-cis-trans* photoisomerizations, (ii) population grating due to triplet states, and (iii) thermal grating.

Molecular reorientation of elongated *trans* molecules, due to multiple *trans-cis* photoisomerizations in solid polymeric matrices, is typically a very slow process ranging from hundreds of ms to minutes [16, 19, 20]. It should be also noted, that taking into account this mechanism, polarization grating recording an so optical phase conjugation signal with *s-p* input wave polarizations of $E^{(1)}$ and $E^{(3)}$ should be observed in our material. In Fig. 6 we can see, that the maximum optical phase conjugation signal could be observed for the same (parallel *s-s*) polarization state of the $E^{(1)}$ and $E^{(3)}$ recording beams decreasing steeply with rotation of $E^{(3)}$ polarization. For orthogonal *s-p* polarization of $E^{(1)}$ and $E^{(3)}$ the phase conjugation signal disappears. Therefore we conclude that in this particular matrix the angular hole burning mechanism can not be considered as the major mechanism inducing refractive index grating.

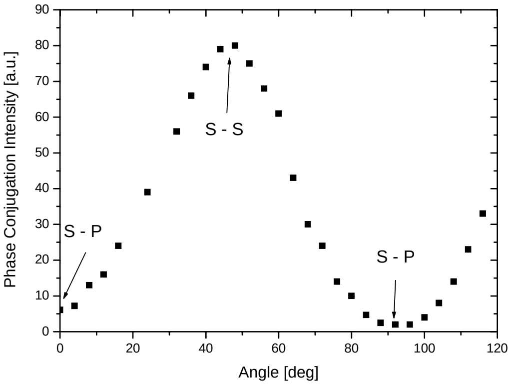

Fig. 6. Changes of the phase conjugation signal intensity in function of polarization state of I_3 beam (here rotation angle of λ/2 plate). Polarizations of I_1 and I_2 were set s while polarization of I_3 beam was rotated by a half-wave retardation plate.

Some previous experimental results, like real-time holography [21] or optical phase conjugation [22-25] in dye doped polymer films, pointed out that an excited-state saturable-absorption population model, based on spatially periodic distribution of DR1 molecules in the T_1 triplet level, was responsible for the fast and reversible refractive index grating formation. Once the writing laser beams are switched off, the triplet-state population grating relaxes with a characteristic time constant τ_T, which is the lifetime of the T_1 triplet state. In our case as can be calculated from the curve presented in Figure 3, the $\tau_T \approx 2.72$ ms for excitation light intensity on average $I = 5.4$ W/cm^2. In this model no permanent alignment of *trans* molecules is invoked and the light scattering on the population grating is usually very weak as the concentration of triplets is limited by concentration of DR1 molecules and triplet lifetime.

Finally, a thermal grating arises when the absorbed optical energy of light is dissipated to the sample. The resultant spatially periodic temperature distribution $\Delta T(x)$ produces periodic density changes $\rho(x)$ of the matrix [26]. The relative change of optical path due to thermo-optic refractive index change and thermal expansion of the sample is described by eq. (6):

$$\frac{\Delta(nL)}{nL} = \frac{1}{n}\frac{\partial n}{\partial T}\Delta T + \frac{1}{L}\frac{\partial L}{\partial T}\Delta T \quad (6)$$

where refractive index *n* and thickness of the sample L can be altered by a local rise in temperature. The decay time constant of the thermal grating should rise quadratically with the grating periodicity Λ:

$$\tau_{th} = \frac{\rho C_p \Lambda^2}{4\pi^2 \kappa} \quad (7)$$

where ρ is the matrix density, C_p is the specific heat and κ is the thermal conductivity of the matrix.

The effective relaxation time, taking the contribution of both mentioned mechanisms into account, can be described by eq (8) [27]:

$$\tau_{eff} = \frac{(a_1 \tau_T^D + a_2 \tau_{th}^D)}{(a_1 + a_2)} \quad (8)$$

where $\tau_T^D = \tau_T / 2$, $\tau_{th}^D = \tau_{th} / 2$. Here a_1 and a_2 are the coefficients representing the relative contributions from each mechanism ($a_1 + a_2 = 1$).

To check whether the decay time constant of thermal grating rises quadratically with the grating periodicity Λ, a typical degenerate two wave mixing experiment was performed, where the dynamics of grating formation was measured as a function of the grating period [28]. However, no dependence of the grating decay time constant on the grating period (Λ within a range of 5 μm to 17 μm) was observed. This result seem to indicate that for the used laser beam intensities, falling within the range of 0 to few W/cm^2, the mechanism based on the concept of the population grating appears more plausible.

5. Conclusions

In conclusion, the optical phase conjugation in biopolymer loaded with a NLO chromophore a DR1, namely in DNA-CTMA-DR1 system, has been observed and characterized. The observed fast dynamics (a single millisecond rise and fall times) of optical phase conjugation signals in this particular matrix makes that it is as a very promising candidate for fast processing of optical information. The main disadvantage is the low diffraction efficiency on recorded gratings. The studied system exhibits an excellent reversibility of the phase conjugate signal generation, with no residual gratings left in the bulk of a material even after few hours of exposure to the action of laser light. The mechanism of dynamic grating formation in such a system is not clarified yet. It seems that the population grating based on the DR1 triplet states is the most straightforward mechanism, but we can not definitively exclude other mechanism, e.g. thermal grating. Further studies of the DNA-CTMA-DR1 system are required.

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