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Natural materials with enhanced optical damage threshold

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ABSTRACT

We report hereby the results of our study on optical damage threshold of DNA and DNA-CTMA thin films, doped with natural chromophores extracts. The films were obtained by spin coating on glass substrates. Their morphology was studied by scanning electron microscopy. Their optical damage threshold, which is an important parameter determining practical application of materials in photonics, was studied using a Q switched Nd:YAG laser, operating at 1064.2 nm with 6 ns pulse duration. The study shows that the doping extracts increase significantly this parameter. In some cases it depends also on the method used to obtain the thin film solutions.

1. Introduction

The next, important, high technology revolution, similar to that we had last century in electronics, is expected to happen in photonics. The importance of this branch of research is best illustrated by UNESCO nominating 2015 as Year of Photonics and Light Technologies. Indeed, with increasing needs for high volume information transmission, image creating and processing, fast and reliable operating systems are to be conceived and realized. Here, photonics brings interesting and adequate solutions. Contrary to the electronics, where fluxes of electrons transmit the information, in photonics this role is played by beams of photons.

Photons are bosons with no electric charge. As a consequence, the beams of photons can cross barriers allowing a high volume parallel processing. There are materials (e.g. high purity fused silica) with very low optical beam propagation losses. In the case of electrons, the propagation losses are high because of the electric charge of the information carrier (an exception to this rule is represented by the costly supraconductors). The commercially available high quality fused silica fibers, with losses of *ca.* 0.2 dB/cm at 1.55 μm wavelength [1], can be considered as “photonic supraconductors”. For this reason exactly, the information is sent presently using near infrared light beams and silica fibers. The small intensity loss for the traveling wave permits the signal transmission on long distances, without any need for amplifiers. This is beneficial not only because of low propagation loss along the optical fibers, but it allows also a simultaneous transmission of a large number of optical beams in the same fiber, differing sufficiently in frequency, to get the necessary information on the transmitted signal. These operations are done by multiplexing (before emission) and demultiplexing (after transmission) the propagating light beams, to collect the whole information sent [2]. The fiber optics communication systems are also much less sensitive to the electro-magnetic perturbations than the electric ones. However, there is a bottleneck which is the existence of an electrical/optical interface, which allows the signal to be transmitted to the traveling information wave carrier. The operation is done *via* the linear electro-optic (Pockels) effect, which permits changes in the bearing beam under the influence of an electric field. More frequently used is a direct traveling beam intensity modulation by varying the intensity of the emitted laser beam through the power supply. The use of non-linear optical (NLO) material will allow the suppression of this slow electro-optic interface by light, becoming thus possible to modify the phase of the propagating beam *via* the optical Kerr effect. Here, the phase is modulated by another light beam through the light induced change of the material index of refraction.

Organic chromophores form a class of materials with the largest known optical Kerr susceptibilities, originating from the enhanced polarisability of conjugated π electrons. A lot of effort was done on synthesizing such molecules. As most of applications in photonics are targeted in waveguiding configuration, materials processable into thin films, with very good propagation properties, are necessary. Because of good light propagation properties, synthetic polymers are used as matrix for the photosensitive chromophores. However, these materials are source for some serious environmental concern, due to their slow degradation. The synthetic polymers have a lifespan of a few hundred years. Also their long-term toxicity, as well as that of synthetic chromophores used to render them photoresponsive, is not well known yet.

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Due to the pollution effects, possible toxicity, as well as an important nowadays attention for durable development, the interest of researchers turned to the nature-made polymers and photosensitive molecules [3–6]. Biopolymers may replace the synthetic materials, bringing subsequently new values. They originate from renewable resources and, if not protected, degrade rapidly. Nevertheless, it has been proven that the deoxyribonucleic acid (DNA) based materials are very interesting biopolymers, with a high potential for application in photonics [3–6]. In particular, a DNA-surfactant complex can be functionalized to obtain interesting NLO properties and is processable into good optical quality thin films [3–6].

Another important parameter concerning the application of thin films in photonics is the optical damage threshold. To obtain an important NLO response, high light intensities are required. This is possible by using the already mentioned optical waveguides where light is confined to small spaces. This confinement leads to a high light intensity, which the used material has to withstand.

In this paper we report our studies on functionalization of DNA and DNA – CTMA (cetyl trimethyl ammonium chloride) complexes with natural extracts (NE) of chromophores, obtained from natural spices: turmeric, paprika and curry leaves. The obtained materials can be processed into good optical quality thin films by the solution casting technique and exhibit high optical damage threshold (ODT). In this study we were interested not only in the thin film optical damage thresholds for different complexes and NE chromophores, but also on their dependence on the preparation method.

2. Materials

2.1. Photosensitive chromophores

The natural dyes are well known for their low toxicity, or the lack of it. Being natural products, they originate from renewable resources and, if not protected, degrade rapidly. Thus their isolation does not require a heavy, often polluting, multi-step synthesis as in the case of synthetic molecules. Natural dyes attract an increasing attention from the food industries [7], from the pharmaceutical sciences to obtain supplements with anti-inflammatory and analgesic effects [8], in chemistry [9] as well as in photonics and electronics.

Among the natural chromophores, the largest interest for their optical properties was attracted by anthocyanines [10–12]. These compounds are present in flowers, in leaves (where they are biosynthesized), as well as in fruits. These molecules exhibit conjugated π electron systems, presenting a very large range of conjugation lengths. For example, blueberries exhibit similar absorption spectrum [13] to that of reference molecule for nonlinear optics, which is Disperse Red 1 (DR1) [14], due to a similar conjugation length. Moreover, anthocyanines are smaller than the synthetic NLO molecules. Therefore, one can expect a larger nonlinear optical susceptibility, because this property is a volume-depending one. Natural chromophores are also studied in view of their application as photosensitizers [15–18] in dye synthesized solar cells (DSSC) [19].

For this study we have chosen, the following nature made chromophores, extracted from the spices, fruits or leaves:

i) Curcumin (Fig. 1a) from turmeric (*Curcuma longa*), known also as Indian safflower, part of the *Zingiberoideae Family*; curcumin is synthesized by the perennial erect plant. Turmeric is used since ancient times as a spice coloring or flavoring agent in food industry, but also for the treatment of several types of diseases in popular medicine [20]. According to the European Pharmacopoeia, turmeric rhizome is an official medicinal product. The turmeric extract contains mainly curcumin as a dye [21].
ii) Capsaicin and capsorubin (Fig. 1b1, b2) from paprika obtained from pepper (*Capsicum annum*), an annual herbaceous plant, part of the *Solanaceae Family*. Peppers are used as dyes, flavors and as a spicy taste source, depending on the processed product. They can be used fresh, dried, frozen, smoked, fermented or as oleoresin extract [22]. The red color of mature fruits is due to several carotenoid pigments, including capsaicin, capsanthin, capsorubin and β-cryptoxanthin which are present as fatty acid esters.

The most important pigments are capsanthin and capsorubin. They represent 30–60% and 6–18%, respectively, of the total carotenoids present in the fruit [22]. Ripe red peppers are widely used as food colorants and they are also a rich source of carotenoid pigments [23].

iii) Karapinchamine A (Fig. 1c) from curry (*Murraya koenigii*), which is an aromatic small tree perennial vegetable. It is a part of the *Rutaceae Family* [24]. Curry leaves and curry leaf oil are exported both from India and from other different parts of the globe for being used as a spice. The plant grows freely in nature, but can also be grown both as ornamental plant and for large-scale use as a spice [25].

Curry leaves contain flavonoids that are responsible for their coloring in green, as well as carotenoids and alkaloids like Karapinchamine A (Fig. 1c) [24].

As seen from Fig. 1 all chromophores are π electron conjugated systems, which are reputed to exhibit large third-order nonlinear optical properties [26]. The maximum absorbance wavelengths of the natural extracts solutions are given in Table 1.

The natural extracts (NE) of chromophores were obtained by the maceration technique of raw material in isopropanol or in butanol solvents, and used as such, without any attempt to isolate the main dye.

The maceration technique is the oldest and simplest method for extraction of chromophores. For that an exact quantity of 4 g of freshly grinded powder of vegetable material was added into a dark flask. 20 mL of solvent (isopropyl or n-butyl alcohol) was added dropwise and the flask was carefully sealed. After that the flask was kept in dark for 72 h. Finally the mixture was filtered and dried. The obtained filtrate was used as such in our experiments.

2.2. Matrix

As a matrix for the NE chromophores, we used the most important, well-known biopolymer which is deoxyribonucleic acid (DNA). DNA has already proved to be a very interesting matrix for synthetic photosensitive molecules, exhibiting promising optical properties [31,32].

DNA consists of 4 nitrogen bases (cytosine, thymine, adenine, guanine), a phosphoric acid residue and a pentose (deoxyribose). DNA and its complex with cetyl-trimethyl ammonium cation (DNA-CTMA) can be processed into good optical quality thin films by the solution spinning method. Moreover the DNA-CTMA complex is insoluble in water, the only solvent for DNA, and soluble in a large class of organic solvents. This property allows functionalization of the complex with dyes that are insoluble in water.

DNA and DNA-CTMA were shown to exhibit large optical damage threshold, larger than for typical synthetic polymers like polycarbonate (PC) or polyethylene glycol (PEG) [33]. Chromophores embedded in exhibit better chemical, thermal and UV degradation stabilities making them interesting materials for application in photonics and in electronics [34].

3. Methods

DNA used in this study was purchased at Chitose Institute of Science & Technology, CIST, Hokkaido, Japan. It was extracted from the waste produced by the salmon processing industry. DNA was dissolved in distilled water and doped with the above mentioned natural extracts. The DNA-CTMA complex, used in this study, was obtained by the reaction of DNA and CTMA in water solution [6,14]. The formed salt DNA-CTMA, as insoluble in water, precipitates and can be easily