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Polylactic acid promotes healing of photodegraded disperse orange 11 molecules

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ABSTRACT

We report on the recovery of a photodegraded organic molecule mediated by a biopolymer. Amplified spontaneous emission (ASE) from disperse orange 11 (DO11) dye-doped polylactic acid (PLA) was used to monitor photodegradation while the material was being damaged by a strong pump laser. The ASE signal fully recovers over two hours time when the pump beam is blocked. The fluorescence spectra was also observed to recover after partial photobleaching the dye-doped polymer. PLA is the first biopolymer known to mediate the recovery of a photodegraded organic dye molecule.

1. Introduction

Many organic molecules have delocalized electrons from conjugated bonds allowing the molecule to interact strongly with ultra violet and visible light. Organic molecules are used in many optics and photonics applications as colorant materials [1], photovoltaic materials [2,3], nonlinear optical materials [4,5], and fluorescent markers [6,7]. The fluorescent molecules with significant Stokes shifts and a high quantum yields are also used as laser gain media [8–10], where laser markers have recently been considered for biomedical imaging [11]. Although organic molecules can perform exceptionally well as optical materials, the intensity dependent photodegradation [12–14] of these molecules is a major drawback of their use in solid-state devices.

Much research has uncovered aspects of photodegradation of organic dyes [15–18]. Placing organic dye molecules in various solid matrices changes the rate of photodegradation [19–21]. Applications such as dye lasers use a large dye-doped liquid reservoir that can be cycled through the laser cell, where the degraded molecules are diluted in the larger bath of optically active molecules to extend the operational lifetime. A phenomenon known as self-healing could potentially be used to create long-lifetime devices made from dye-doped polymer materials [22].

The first reported case of self-healing of an organic dye in a polymer matrix was by Peng et al. for rhodamine B-, fluorescein-, and pyrromethene-doped poly-methyl-methacrylate (PMMA) polymer optical fibers [23]. The anthraquinone dye, disperse orange 11 (DO11), was later placed in a host matrix of PMMA to create a self-healing material that fully recovers after severe photodegradation has occurred [24]. It was shown that dye diffusion was not a contributing factor to the self-healing phenomenon in DO11-doped PMMA [25]. Orientational hole burning was also shown not to be a mechanism of the degradation and recovery process in DO11-doped PMMA [26]. DO11 was shown to degrade with a slow recovery rate in polystyrene (PS), and the degree of recovery

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increases for DO11-doped PMMA/PS copolymers when the concentration of PMMA increases [27], where over an order-of-magnitude reduction in the recovery rate of photodegraded DO11 in pure PS was reported relative to the recovery rate in pure PMMA [28]. No recovery from a photodegraded state is observed when DO11 is dispersed in a methyl methacrylate (MMA) monomer solution [29]. Thus, interactions between DO11 molecules in a solid matrix alone appear to self-heal while some polymer structures can also mediate an expedited recovery.

Studies of DO11-doped PMMA, since its discovery as a self-healing material, seek to elucidate the effects of external electric fields [30], temperature [31], concentration [26], pump wavelength [32], and sample geometry [33] on the rate of healing. PMMA was the only polymer matrix known to mediate the healing of only a few organic dyes until 2015, when Anderson et al. showed that a degraded random laser with a rhodamine 6 g dye-doped polyurethane (PU) gain medium also underwent self-healing as revealed via the restoration of the laser's output power [34]. A self-healing random laser was also created by distributing ZrO_2 nanoparticles into a DO11-doped PMMA matrix [35]. Many anthraquinone dyes have recently been reported to either partially or fully recover their optical properties after being photodegraded by a pump beam [36]. Recently, the phenomenon of self-healing from photodegradation has been observed from photocurrent measurements in perovskite solar cells [37].

In this paper, we report on the degradation and recovery of the amplified spontaneous emission (ASE) of DO11-doped polylactic acid (PLA). After the ASE signal drops by more than 50% during photodegradation, we observe that it fully recovers within a few hours in the dark. As in Ref. [24] the ASE signal was actually found to recover beyond its initial brightness. Greater than unity recovery of ASE emission is a well-known phenomena. This increase in output intensity relative to the initial output has also been observed in a self-healing random laser [38]. Irreversible changes (such as some types of thermally induced changes) to the polymer matrix when irradiated by the pump beam may contribute to the greater than 100% recovery [39].

2. Experiment

Films of 2 wt. % DO11-doped PLA were made by dissolving 10 wt. % solids in tetrahydrofuran, and drop casting onto clean glass slides. A glass cover was placed over the films to slow the drying process immediately after the solution was dropped onto the slides. After 30 min, the films were placed in an oven at 130 °C and annealed for one hour.

The DO11-doped PLA films were pumped with a Continuum Minilite II laser operating at a wavelength of 532 nm with a pulse duration of 5 ns. The pump beam energy was approximately 250 μJ, where the pump beams stability was monitored using an Ophir pyroelectric detector as shown in Fig. 1(a). The chemical structures for DO11 and PLA are shown in Fig. 1(b).

The pump beam was expanded through two collimating lenses, which was focused to a thin line using a cylindrical lens as shown in Fig. 1(a). The pump beam profile was taken by placing a 550 nm long wavelength pass filter over a CMOS camera and collecting the fluorescence profile next to marks identifying the length scale on the film. The highly eccentric pump beam profile shown in Fig. 1(c) had a semi-major axis of 2.5 mm and a semi-minor axis of 100 μm for the Gaussian widths ($1/e^2$) of the elliptical beam spot. The electric field polarization of the pump beam was aligned with the semi-minor axis of the beam profile.

The ASE was focused onto the end of a fiber that feeds into an Ocean Optics USB650 spectrometer. We used an integration time of 0.9 s while collecting the data from the spectrometer's CCD array,

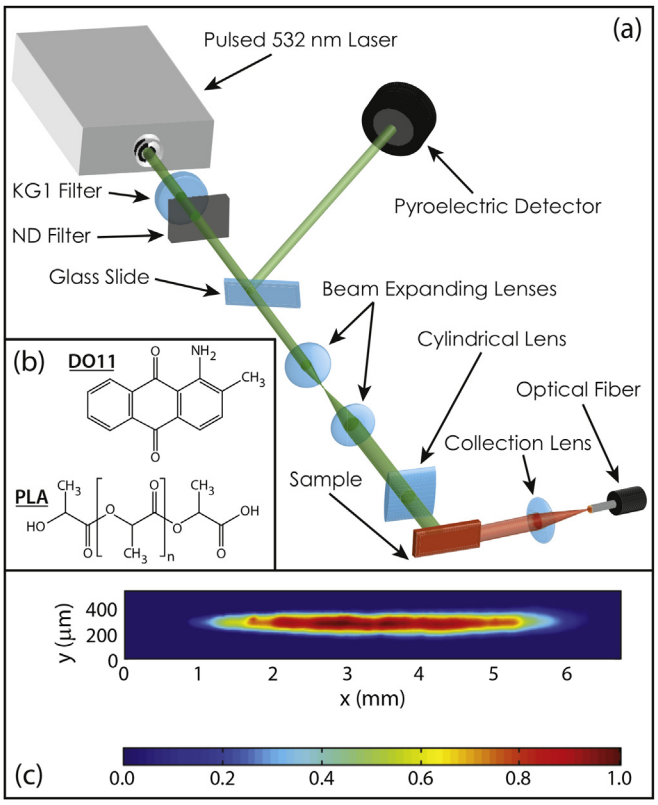

Fig. 1. (a) Diagram of photodegradation experiment. (b) Chemical structures for DO11 and PLA. (c) The pump beam profile captured from fluorescent imaging on the DO11-doped PLA sample.

which corresponds to averaging the normalized signal over 9 pulses from the pump operating at 10 Hz.

The recovery data was collected by the spectrometer in sparsely separated pump intervals. Spectra were recorded for 30 s pump intervals (with single measurements integrated over 0.9 s) followed by an average of all integrated ASE spectra over the 30 s interval. The time between successive measurements for the recovery data was also increased as the sample began to recovery so as to further reduce degradation.

3. Discussion

The reasonably high quantum efficiency and large Stokes shift of DO11 makes the molecule a good candidate for dye lasers, where its properties as a laser gain medium have been previously reported [40]. As typical with organic molecules, pumping a population of DO11 into an excited state leads to dye photodegradation, by which we mean the muting of optical phenomena associated with the original optical resonance. ASE is a nonlinear function of both the dye concentration and the pump fluence, thus these measurements are ideally suited to studying the effects of population degradation and recovery on the gain for laser applications. Concentration dependent recovery times have been observed for self-healing optical materials [26].

For a circular beam spot, we observed a broad fluorescent signal at low pump intensity. An ASE peak began to protruded from the fluorescence profile as the pump intensity was increased. The ASE amplitude quickly dominated the fluorescence spectrum at high power. The beam spot was changed to a highly eccentric shape using a cylindrical lens for the degradation and recovery experiment to produce a strong ASE signal using a relatively low fluence.