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Nonlinear optical transmission of cyanobacteria-derived optical materials

Edward H. Zhao [a], Fumiya Watanabe [b], Wei Zhao [a,*]

[a] Department of Chemistry, University of Arkansas at Little Rock, 2801 South University Avenue, Little Rock, AR 72204, USA
[b] Center for Integrative Nanotechnology Sciences, University of Arkansas at Little Rock, 2801 South University Avenue, Little Rock, AR 72204, USA

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ABSTRACT

Cyanobacteria-derived optical materials for optical limiting applications have been studied in this work. Six samples have been prepared from cyanobacteria including cyanobacteria suspension in water, extracts in water, methanol, and N,N-dimethylformamide, and pyrolyzed cyanobacteria (PCYB) dispersed in dsDNA (sodium salt from salmon testes) solution and sodium dodecyl sulfate solution, respectively. The extracts contain phycocyanin, chlorophyll *a*, and carotenoids as measured by optical absorption spectroscopy, while the PCYB is a nanostructural composite composed of multi-walled carbon nanotubes, carbon nanoringes, and multilayer graphenes, as revealed by transmission electron microscopy. The optical limiting responses of the samples have been measured at 532 and 756 nm. The PCYB in dsDNA solution has the best limiting performance out of all the cyanobacteria-derived samples. It outperforms carbon black suspension standard at 532 nm and is a broadband limiter, which makes it attractive for optical limiting applications.

1. Introduction

Generation of novel substances from natural sources such as plants and microorganisms is one of effective approaches to achieve the goal of sustainability for a broad range of applications including photonics [1]. Recent examples of the substances include cellulose nanocrystals and nanofibrils produced from trees, bacteria and some marine animals [2,3], and biofuels extracted from cyanobacteria [4]. Both sources of trees and cyanobacteria harvest sun energy and reduce carbon dioxide emission by carbon fixation. In particular, cyanobacteria have recently emerged as an attractive bioenergy resource [4], in addition to their traditional role such as a source of natural colorants [5]. In this work, we study cyanobacteria-derived materials for photonic applications [1,6]. By focusing on measuring the pigments and carbon nanostructures derived from cyanobacteria, low cost laser limiting materials [6,7], the materials that can limit the powerful laser intensity for eye and sensor protection, may be realized.

Lasers are being used everywhere for many purposes including nuclear fusion and eye surgery since the invention of the first functioning laser more than 50 years ago [8]. Because lasers are now being used as weapons [9], the need for protection from lasers increases. Optical limiting is a property of some materials with which at a low laser power, the transmitted power increases linearly. However, at a certain laser input power, the transmitted power stops increasing [7,10–12]. The current optical limiting materials include C_{60} solution in toluene [10,11] and carbon black aqueous suspension [13,14], which are the benchmark standards of optical limiting materials [11]. However, they have some disadvantages [15]. Carbon black suspension is unstable and tends to form aggregates. C_{60} solution is a good limiter at 532 nm, but it is not a broadband limiter. Finding new optical limiting materials with better limiting properties is under intense exploration.

Cyanobacteria are very abundant organisms [16], accounting for more than 25% of the net primary productivity in oceans [17]. They are photosynthetic, containing pigments like chlorophyll *a*, β-carotene, and phycobiliproteins. Many of optical limiting materials are usually pigments that absorb at certain wavelengths, making them work through various nonlinear optical mechanisms, including two photon absorption (TPA), reverse saturable absorption (RSA), nonlinear refraction, and nonlinear scattering [6,10,11,13,14,18,19]. Interestingly, cyanobacteria possess unique acclimative responses, complementary chromatic acclimation, for altered pigment synthesis when grown under controlled light colors [17]. A recent study has found that by using far-red light for growth, cyanobacteria have produced pigments with enhanced absorption in far-red light [17], making them a good candidate for optical limiting applications in this light region. For photonic applications, in the past decades, there have been a number of

* Corresponding author. Tel.: +1 501 569 8823.
E-mail address: wxzhao@ualr.edu (W. Zhao).

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reports about plant-derived pigment substances. For example, unseparated plant pigments [20], chlorophylls, and their derivatives [21] exhibited laser action. Third order nonlinear optical susceptibilities of a series of natural pigments, carotenoids [22] and chlorophyll *a* and *b* [23], extracted from spinach have been measured. A few reports about the optical limiting performance of chlorophyll *a* derived from plants were also published [24,25]. However, in view of the fact that cyanobacteria also contain a high carbon level in the pigment molecules and cell walls, when carbonized, they might form unique carbon nanostructures. These carbon nanostructure-based composites might have superior nonlinear optical properties as carbon nanotubes [11,26,27] and graphene [15,28–33] do, and might be used as a low cost broadband limiter. To our knowledge, however, no systematic work has been done to explore this opportunity. In this work, the cyanobacterial cells, the extracts from the cells, and the carbonized cyanobacteria by pyrolysis have been studied for laser limiting properties. The results indicate that the pigment molecules have optical limiting responses at selected wavelength 532 nm, but not at 756 nm, suggesting not a broadband limiter. While as anticipated, pyrolyzed cyanobacteria (PCYB) samples have unique carbon nanostructures, exhibiting optical limiting responses superior to carbon black suspension. They may serve as low-cost, attractive broadband limiting materials for laser protection applications.

2. Experimental

2.1. Materials

Water soluble carbon black was purchased from Acheson Colloids Co. Fullerene C_{60} (99.5 + % pure) was from Lancaster Synthesis Ltd. Reagents including double-strand DNA (dsDNA) (sodium salt from salmon testes), sodium dodecyl sulfate (SDS, purity > 99%), tris(hydroxymethyl)-aminomethane (Tris, >99.9%), N,N-dimethylformamide (DMF, 99.9 + %), and toluene (99.9 + %) were purchased from Sigma–Aldrich. Methanol (HPLC grade) was from Fisher Scientific. The buffer solution was Tris buffer (10 mM, pH 8.0). The wild-type of cyanobacterium Synechocystis sp. PCC 6803 over mid-logarithmic growth phase in BG-11 cell culture medium was from the group of He [34].

2.2. Preparation of cyanobacteria-derived samples

The cyanobacterial cells (absorbance $A = \sim 0.6$ at 730 nm in 1 cm cuvette) were collected in a 150 mL vial using a centrifuge at a speed of 500 rpm for 5 min to remove the cell culture medium. The cells were re-dispersed in deionized (DI) water and centrifuged. The supernatant at the top was removed. The cells were washed two more times and the purified cyanobacteria were dispersed in DI water in whole cells ($\sim 3 \times 10^6$ cells/mL, based on $A = 0.33$ at 730 nm in 1 cm cuvette [35]). To prepare the extracts of cyanobacteria in different organic solvents, the purified cyanobacteria were harvested in a microfuge vial and resuspended in 1 mL methanol or DMF. After vigorously shaking, the mixture was centrifuged in a microcentrifuge (VWR Galaxy 16 Microcentrifuge) at a speed of 14,000 rpm for 5 min. The supernatant was collected, which contained the pigments, such as chlorophyll *a*. For the extract in water, the cells were first ground to break up the cell walls to release the pigments, then the same procedure as used in organic solvents was repeated to extract the pigments using DI water. The extracts were diluted with the solvents so that the linear transmittance is about 40–50% at 532 nm with a path length of 1 cm. The pigment concentrations in the extracts were photometrically determined [34,36–38]. The methanol extract contained ~35 μg/mL chlorophyll *a* and ~13 μg/mL total colored carotenoids, while the DMF extract contained ~46 μg/mL chlorophyll *a* and ~18 μg/mL total colored carotenoids [34,36]. For the extract in water, it contained ~0.4 mg/mL phycocyanin and ~15 μg/mL mycosporine amino acid-like compounds (molar absorptivity 106,500 $M^{-1}cm^{-1}$ for phycocyanin [38] and 43,800 $M^{-1}cm^{-1}$ for mycosporine amino acid-like compounds [37]).

To prepare pyrolyzed cyanobacteria (PCYB) suspensions, the harvested cyanobacteria were placed in a Lingberg/Blue HTF55000 series hinged tube furnace under helium protection. The furnace temperature was kept at about 380 °C for about 1 h for pyrolysis. After cooling, the black substance, PCYB was collected. About 1 mg of PCYB were dispersed into 5 mL of dsDNA solution (2 mg dsDNA/mL) in pH 8.0 Tris buffer [15,39,40] and 5 mL of 1 wt% SDS aqueous solution [15,41,42], respectively, with an aid of sonication in a Branson 1510 ultrasonicator. For benchmark optical limiting standards, a saturated C_{60} solution was prepared in toluene, and carbon black (~0.1 mg) was dispersed into 5 mL of 1 wt% SDS aqueous solution with the assistance of sonication. The suspensions were prepared with necessary dilution so that the linear transmittance T_L is ~40–60% at 532 nm at an optical path length of 1 cm.

2.3. Sample measurements

The absorption spectra of the suspensions were measured using a Varian Cary 5000 UV–Vis–NIR spectrophotometer with 1 mm quartz cuvettes. The transmission electron microscopy (TEM) measurement was performed using JEM-2100F transmission electron microscope for PCYB samples. A few drops of TEM sample solution were dripped on holey carbon coated copper TEM grids (SPI Supplies) to dry before being inserted into the TEM. To minimize the electron beam damages, the samples were imaged at 80 kV.

For optical limiting measurements, the laser system used in the experiments was a Continuum Powerlite Precision II Series Model 8000 Injection Seeded Nd: YAG nanosecond pulsed laser with 8 ns pulse duration and $\lambda = 1064.2$ nm output [15]. The laser was used to pump two LaserVision optical parametric oscillators and optical parametric amplifier systems to generate two adjustable laser beams covering 532 nm, 710–910 nm, and 1.06–5 μm [43–46]. Here, two laser beams of wavelength 532 nm and 756 nm were used to examine the optical limiting properties of the samples.

The optical limiting measurements were conducted by using the method described in Ref. [15]. The transmittance T was then measured as a function of laser incident fluence, at least 3 times at each input fluence for each sample. The average standard deviation was less than 10% for all data sets. The collected data were analyzed by plotting output fluence as a function of input fluence. The results were compared with those of carbon black suspension and C_{60} solution in order to evaluate the effectiveness. For comparison, the linear transmittance T_L is normalized to 1 for plotting the figures. In order to determine the limiting threshold, which is defined as the input power at 50% of the linear transmittance, the normalized nonlinear transmittance of PCYB samples was also plotted as a function of input fluence. The optical limiting mechanisms were also examined by fitting selected data with a RSA equation [47–49] for cyanobacteria extract samples and a TPA equation [15,50] for PCYB samples.

3. Results and discussion

Fig. 1 shows various substances made from cyanobacteria. The cyanobacterial extracts in different solvents have different colors because different pigments such as chlorophyll *a*, β-carotene, and phycobiliproteins inside of the cyanobacteria are released. The PCYB sample becomes black after pyrolysis.