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Nonlinear optical properties and supercontinuum spectrum of titania-modified carbon quantum dots

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Abstract. **We have studied the nonlinear optical properties and supercontinuum spectrum of solutions of carbon quantum dots prepared by a hydrothermal process from chitin and then coated with titania. The titania coating has been shown to have an activating effect on the carbon quantum dots, enhancing supercontinuum generation in the blue-violet spectral region and enabling their nonlinear optical characteristics to be varied.**

Keywords: *carbon quantum dots, nonlinear refractive index, filamentation, supercontinuum, femtosecond pulses.*

1. Introduction

Carbon quantum dots (CQDs) are a new class of carbon nanoparticles, along with unique nanostructures such as fullerenes, nanotubes, graphene and nanodiamond. They were obtained first in the course of purification of single-wall carbon nanotubes by electrophoresis in 2004 [1] and later by laser ablation of graphite powder [2]. CQDs are discrete carbon nanoparticles that have some similarity to and fundamental distinctions from nanodiamond [3, 4]. In contrast to other carbon materials, they possess photoluminescence properties [1]. According to a number of studies, their photoluminescence is due to exciton recombination at surface energy traps [2]. The peak position and intensity of the broadband emission from CQDs in the visible range can be matched to the excitation wavelength by adjusting their size, the synthesis process and the functional groups covering their surface [5]. Considerable attention has recently been paid to photoinduced electron transfer in CQDs, their redox properties [6] and their biocompatibility [7].

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Owing to their unique properties and great potentialities, CQDs are being used increasingly in biomedicine, optoelectronics, catalysis, biosensors and other applications. CQDs are assumed to have nonlinear optical properties, which depend significantly on the passivation of their surface, the nature of the organic residues (radicals) used, the CQD size and, possibly, the synthesis process [8, 9]. However, research in this direction has only been reported for nano- and picosecond pulses [10]. The purpose of this work was to study the nonlinear optical properties and supercontinuum (SC) spectrum of CQD solutions under excitation with femtosecond laser pulses.

2. Experimental

CQDs were synthesised from chitin by a hydrothermal process, as described by Shchipunov et al. [11]. Their surface was modified with titania via mineralisation, a method proposed for soluble polysaccharides and cellulose [12, 13]. The CQD size ranged from 2 to 4 nm. The samples prepared in this study are listed in Table 1.

Table 1. CQD samples.

Sample	Percentage of CQDs	Preparation technique
CD1	0.058	Hydrothermal synthesis from shrimp chitin at a temperature of 180 °C for 18 h
CD2	0.1	Hydrothermal synthesis from lobster chitin at a temperature of 180 °C for 22 h
CDTi1	0.058	Treatment of the shrimp chitin-derived CQDs with titania
CDTi2	0.058	Treatment of the shrimp chitin-derived CQDs with a triple amount of titania

To study the spectral characteristics of SC generation in the samples and their nonlinear properties by the *z*-scan technique, we used experimental setups described elsewhere [14, 15], which were supplemented with a harmonic generator and dual-wavelength mirrors (for wavelengths λ = 400 and 800 nm). The pulse duration at λ = 800 nm was 45 fs and the pulse energy did not exceed 5 mJ. The pulse duration at λ = 400 nm was 85 fs and the pulse energy did not exceed 1 mJ.

The fluorescence spectra of the samples under single- and two-photon excitation are presented in Fig. 1, and their transmission spectra, in Fig. 2. We studied the filamentation of femtosecond 800-nm laser pulses of ~45 fs duration in the samples. The SC generation threshold in CD1 is roughly equal to that in distilled water (measurement accuracy of 5%

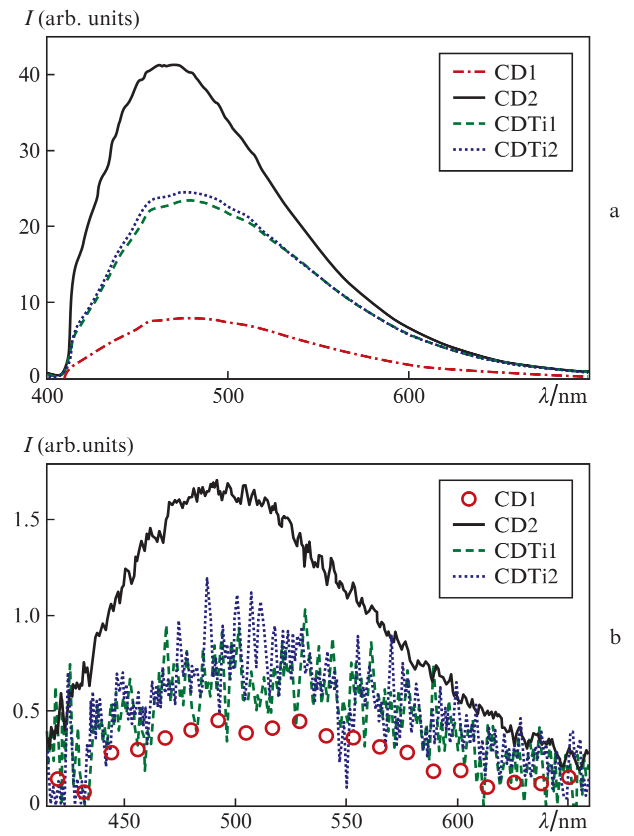

Figure 1. Fluorescence spectra of the samples under (a) single-photon excitation at λ = 400 nm and (b) two-photon excitation at λ = 800 nm.

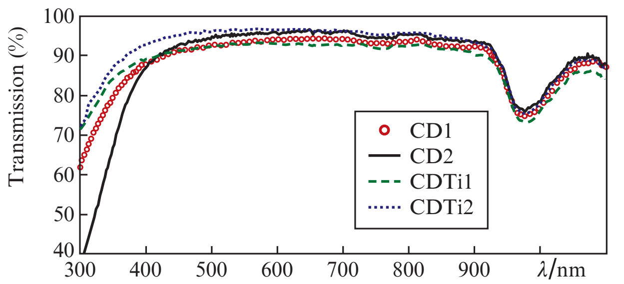

Figure 2. Transmission spectra of the samples at an optical thickness of 5 mm.

or better), and the threshold in CDE2 is ~10% higher. The threshold in the CDTi1 and CDTi2 samples is 15% lower than that in distilled water.

Figure 3 shows the SC spectra of the samples in the visible range. Among the samples studied, the titania-activated samples CDTi1 and CDTi2 have a higher SC yield in the blue spectral region. The variation from the unmodified CQDs is about 20%.

Using the z-scan technique, we measured the nonlinear refractive index n_2 and the nonlinear absorption coefficient β of the samples under excitation at λ = 800 and 400 nm in a 1-mm-thick cuvette. The measurement results are presented in Table 2.

It is seen from Table 2 that the nonlinear refractive indices of the CQD solutions and solvent under IR excitation are almost identical and that the nonlinear absorption coefficients of the CQD solutions are markedly smaller. Under

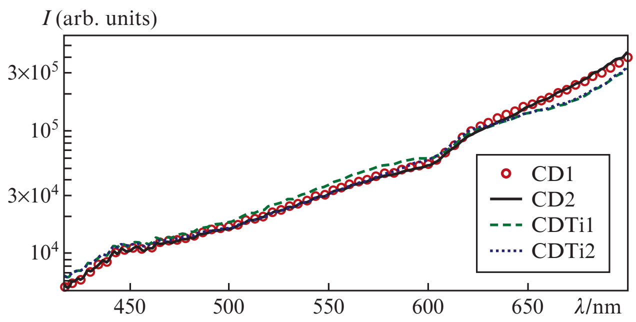

Figure 3. SC spectra of the samples.

Table 2. Measured nonlinear optical characteristics of the samples.

Sample	Excitation wavelength/nm			
	800		400	
	$n_2/10^{-16}$ cm^2 W^{-1}	$\beta/10^{-12}$ cm W^{-1}	$n_2/10^{-16}$ cm^2 W^{-1}	$\beta/10^{-12}$ cm W^{-1}
CD1	2.0±0.2	4.7±0.5	2.6±0.3	6.6±0.7
CD2	2.3±0.2	3.7±0.4	5.2±0.5	8.8±0.9
CDTi1	1.9±0.2	4.2±0.4	3.2±0.3	7.9±0.8
CDTi2	2.0±0.2	2.5±0.2	2.4±0.2	6.8±0.7
Distilled water	2.0±0.2	5.8±0.6	2,8±0.3	6,5±0.7

excitation with violet light, the coefficients β of the samples exceed that of the solvent, whereas the behaviour of the nonlinear refractive index is not so unambiguous. The nonlinear refractive indices of the CD1 and CDTi2 samples are slightly lower than the n_2 of the solvent, whereas those of CD2 and CDTi1 exceed it.

3. Conclusions

Titania coating has been found to have an activating effect on CQDs, considerably raising their fluorescence yield, with no significant changes in their nonlinear optical properties. This activation enhances SC generation in the blue spectral region. Our z-scan measurements demonstrate that the nonlinear optical characteristics of solutions of new, CQD-based nanostructures under IR excitation (at λ = 800 nm) are similar to those of the solvent (distilled water). According to recent studies in which picosecond pulses at λ = 1064 and 532 nm were used for excitation [10], the addition of CQDs considerably reduces the nonlinear refractive index n_2 of solutions relative to the solvent. Under excitation at λ = 400 nm, the behaviour of the n_2 of our samples differs from that under IR excitation: the nonlinear refractive indices of CD1 and CDTi2 are lower than the n_2 of the solvent, whereas those of CD2 and CDTi1 exceed it. Surface activation of the CQDs with titania allows their nonlinear optical characteristics to be varied.

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