Optical Materials 76 (2018) 335–343

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Characterization and enhanced nonlinear optical limiting response in carbon nanodots dispersed in solid-state hybrid organically modified silica gel glasses

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ARTICLE INFO

Article history:
Received 23 November 2017
Received in revised form
25 December 2017
Accepted 26 December 2017

Keywords:
Sol-gel processes
Carbon nanodots
Nanocomposites
Optical limiting properties
Silicate

ABSTRACT

Freely dispersed carbon nanodots (CNDs) were introduced into a 3-glycidoxy-propyltrimethoxysilane modified silicate gel glass (i.e. an organically modified silica or ORMOSIL) by a highly efficient and simple sol-gel process, which could be easily extended to prepare functional molecules/nanoparticles solid state optoelectronic devices. Scanning electron microscope imaging, Fourier transform infrared spectroscopy, pore structure measurements, ultraviolet–visible spectroscopy, and fluorescence spectroscopy were used to investigate the surface characteristics, structure, texture, and linear optical properties of the CND/SiO_2 ORMOSIL gel glasses. Images and UV/Vis spectra confirmed the successful dispersion of CNDs in the ORMOSIL gel glass. The surface characteristics and pore structure of the host SiO_2 matrix were markedly changed through the introduction of the CNDs. The linear optical properties of the guest CNDs were also affected by the sol-gel procedure. The nonlinear optical (NLO) properties of the CNDs were investigated by a nanosecond open-aperture Z-scan technique at 532 nm both in liquid and solid matrices. We found that the NLO response of the CNDs was considerably improved after their incorporation into the ORMOSIL gel glasses. Possible enhancement mechanisms were also explored. The nonlinear extinction coefficient gradually increased while the optical limiting (OL) threshold decreased as the CND doping level was increased. This result suggests that the NLO and OL properties of the composite gel glasses can be optimized by tuning the concentration of CNDs in the gel glass matrix. Our findings show that CND/SiO_2 ORMOSIL gel glasses are promising candidates for optical limiters to protect sensitive instruments and human eyes from damage caused by high power lasers.

1. Introduction

Since the advent of the laser in 1960, this technology has been widely used in many fields including medicine, information technology, accurate measuring, chemistry, material processing, material preparation, and in military applications [1–3]. Consequently, interest has also been aroused for the development optical limiting (OL) materials, which feature a decreased transmittance for high intensity laser inputs. Such materials can be used to protect eyes and sensitive instruments from laser induced damage. Over the past decade, considerable efforts have been devoted to the development of ideal broadband OL materials based on mechanisms such as nonlinear scattering (NLS) and nonlinear absorption (NLA) [4–12]. Strong OL activity has been observed in a wide range of materials, including organic dye molecules (e.g., porphyrins [4] and phthalocyanines [5]), high molecular polymers (e.g., polythiophenes [6] and polyanilines [7]), metallic [8] and semiconducting nanoparticles [9], and carbon nanomaterials [10–12]. Among these materials systems, carbon-based nanomaterials, including fullerenes, carbon nanotubes (CNTs), graphene, and carbon black, show excellent potential for use as OL materials and have been widely applied in the field of nonlinear optics. For example, CNTs exhibit unique broadband OL properties from visible to near infrared wavelengths, in the nanosecond regime, owing to NLS from scattering centers consisting of solvent bubbles and ionized carbon microplasma.

Carbon nanodots (CNDs) have emerged as a particularly interesting carbon nanomaterial, which has drawn considerable attention owing to its unique properties, including: excellent chemical and photostability, biocompatibility, easy functionalization, and

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https://doi.org/10.1016/j.optmat.2017.12.051
0925-3467/

up-conversion of photoluminescence. These features have been applied in fields such as bioimaging, solar light harvesting, chemical and biochemical analysis, photocatalysis, and optoelectronics [13–15]. Notably, CNDs have recently been shown to exhibit excellent nonlinear optical (NLO) and OL responses [16–19]. Liang et al. found that the third-order nonlinear susceptibility $\chi^{(3)}$ of CNDs is strongly dependent on the diameter of the CNDs and the carboxyl groups on the surface of the CNDs [16]. Li et al. investigated the third-order nonlinear optical response of CNDs with single 190-fs laser pulses and revealed that nonlinear reflection and absorption were associated with the concentration of CNDs [17]. Dezhi et al. observed strong OL effects in CNDs with an energy threshold of 74 mJ/cm^2 for 800-nm femtosecond laser pulses; the OL effects of CNDs were mainly attributed to two-photon absorption [18]. All these reports confirmed that CNDs are a potential candidate OL material, which can be applied in nonlinear optics. However, many of the above studies were performed in solvent. Although liquid matrices are convenient for investigations of material properties and mechanisms of phenomena, solutions measurements are not generally representative of the practical environment in devices and other applications. Rather, solid-state measurements are of greater utility for preparing device components and for studying underlying optoelectronic mechanisms. Therefore, the incorporation of the CNDs into solid matrices is important for practical applications of the materials.

In the present study, we report a highly efficient and convenient sol-gel synthesis of transparent ORMOSIL gel glasses incorporating well-dispersed CNDs (as shown in Scheme 1). This approach could be easily extended to prepare functional molecule/nanoparticle solid state optoelectronic devices. The additive 3-glycidoxypropyltrimethoxysilane [$CH_2OCHCH_2O(CH_2)_3Si(OCH_3)_3$, GPTMS] helped to improve the elasticity and flexibility of the resultant gel glass and 3-aminopropyltriethoxysilane [$NH_2(CH_2)_3Si(OC_2H_5)_3$, APTES] acted as a weak organic basic catalyst to promote polycondensation. Transmission electron microscope (TEM) and scanning electron microscope (SEM) imaging, Fourier transform infrared (FT-IR) spectroscopy, pore structure measurements, ultraviolet–visible (UV–vis) spectroscopy and fluorescence spectroscopy were performed to investigate the morphology, structure, texture, and linear optical properties of the CND/SiO_2 ORMOSIL gel glasses. The NLO properties of the CNDs in water and OMOSIL gel glass were investigated with the use of a nanosecond open-aperture (OA) Z-scan technique at 532 nm. The results were compared and possible mechanisms for the enhancement of OL behavior of the CNDs in the ORMOSIL gel glass were explored.

2. Experimental

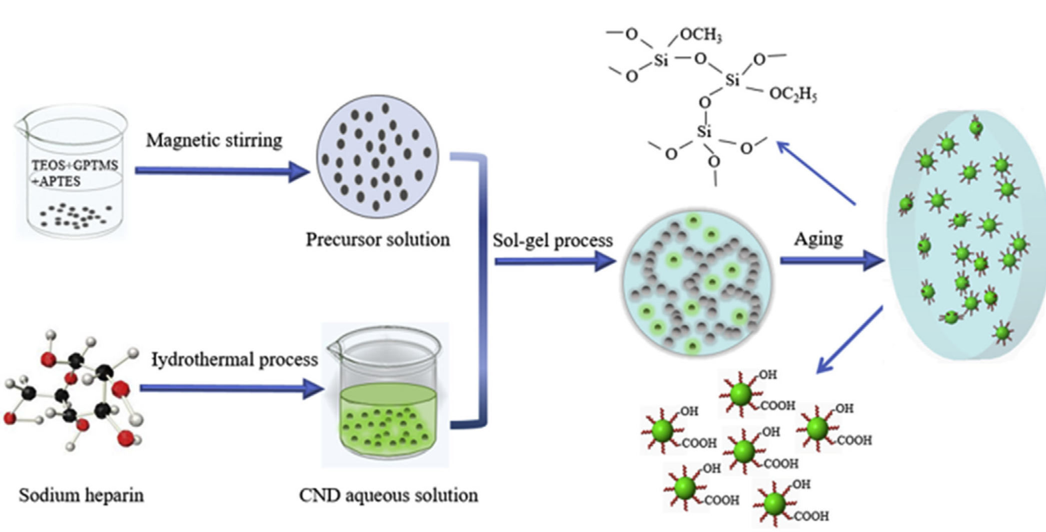
2.1. Synthesis of CNDs

CNDs were prepared by a hydrothermal synthesis using heparin sodium as a raw material. A 40-mL portion of 0.0275 g/mL sodium heparin solution was added to a 50-mL stainless-steel autoclave and reacted in an oven for 12 h at 140 °C. The reacted black mixture was filtered and the filtrate was centrifuged at 10000 rpm for 10 min at 23 °C. After vacuum filtration (filter membrane: 0.22 μm) and dialysis (MWCO = 3500/8000) a light brown supernatant was obtained. The dialyzed solution was then dried in a drying air oven for 48 h (60 °C) to obtain a concentrated CND solution. The solution was further dried to obtain the CND powder.

2.2. Synthesis of CND/SiO_2 ORMOSIL gel glasses

Optically transparent CND/SiO_2 OMOSIL gel glasses were fabricated through hydrolysis and polycondensation of tetraethyloxysilane (TEOS), GPTMS, and APTES. The doping levels of CNDs were 5.5×10^{-4}, 7.4×10^{-4}, 11.1×10^{-4}, and 14.8×10^{-4} (mass ratio of CND powder to SiO_2). The molar ratio of (TEOS+GPTMS+APTES), ethanol, and distilled water in the precursor was 1:4:4; the molar ratio of TEOS, GPTMS, and APTES was 7:2:1. In addition, *N*,*N*′-dimethyl formamide (DMF) was introduced as a solvent and drying control chemical additive at a proportion of 0.6 DMF per ethanol volume ratio. Specifically, 10, 2.65, 1.4, 15, and 4.5 mL of TEOS, GPTMS, APTES, ethanol, and water were respectively mixed by ultrasonication for 30 min. Subsequently, 5 mL of a DMF suspension containing different contents of CNDs was gradually added to the mixture, which was then ultrasonicated for 4 h. The resulting mixture was divided into several parts of equal volume, each of which was individually cast in a polystyrene cell, sealed, and left to age and dry for several weeks. All the gel glasses were approximately 1.3 mm thick and 2.5 cm in diameter.

For comparison, graphene oxide (GO) doped silica (GO/SiO_2) gel glass was also prepared following a similar synthetic procedure to that for the CND/SiO_2 gel glass except that 5 mL of a DMF suspension containing GO was introduced.



Scheme 1. Synthesis of transparent ORMOSIL gel glasses incorporating well-dispersed CNDs.