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# Nonlinear optical responses of carbon quantum dots anchored on graphene oxide hybrid in solid-state transparent monolithic silica gel glasses

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ABSTRACT

Exploring the nonlinear optical (NLO) response of graphene-based hybrids in solid-state three-dimensional macrostructures is vital to promote the practical development of graphene-based photonic and optoelectronic devices. Here, a solid-state hybrid of ultrafine and well-dispersed carbon quantum dots (CQDs) supported on graphene oxide (GO) was chosen as representative of such materials. The hybrid was introduced into organically modified silica gel glasses using a facile sol-gel wet chemical technique to obtain stable transparent monolithic nanocomposites, and their practical application in nonlinear optics was explored. The NLO performances were investigated by the open-aperture (OA) and closed-aperture (CA) Z-scan techniques in the nanosecond regime using a laser with a wavelength of 532 nm. The as-prepared CQD/GO $SiO_2$ gel glasses displayed completely different NLO behavior from that of a CQD/GO suspension. The NLO performance of CQD/GO significantly improved after incorporation into $SiO_2$ gel glasses because of the more graphitized structure of the CQD/GO hybrid. Both the OA and CA Z-scan patterns suggested that the NLO properties of the CQD/GO suspension combined nonlinear absorption and nonlinear scattering, while the NLO response of the CQD/GO $SiO_2$ gel glasses stemmed primarily from nonlinear absorption and nonlinear refraction. In addition, this is the first report of the third-order nonlinear susceptibility $\chi^{(3)}$ of a CQD/GO hybrid doped in solid-state gel glasses. The present results therefore demonstrate the feasibility and versatility of CQD/GO silica gel glasses, a promising new class of highly efficient NLO materials that can be applied in optical communications, radiofrequency optoelectronics, and all-optical signal processing.



## 1. Introduction

The rapid development of laser technology has greatly promoted its application in fields including scientific research, production and processing, medicine, and the military. However, high-intensity laser beams have the potential to harm the eyes, bare skin, photoelectric detection sensors, and sophisticated optical instruments. Therefore, the design and manufacture of laser protection devices has become a central theme of laser technology. Over the last few decades, many efforts have focused on the search for so-called optical limiting (OL) materials, which exhibit "nonlinear extinction"; i.e., they strongly attenuate intense, potentially dangerous laser beams, while readily transmitting low-intensity ambient light. The rapid development of nanoscience and nanotechnology is opening up new opportunities in the synthesis of OL materials, as well as the research and design of practical optical limiters. A variety of materials, ranging from organic dyes (such as phthalocyanine, porphyrin, and fullerene) [1–3], carbon nanomaterials (including carbon black, carbon nanotubes, and graphene) [4–6] to noble metal nanoparticles [7,8] and quantum dots [9,10], have been extensively investigated for their OL effects. Despite significant progress in the past decade in the development of OL nanomaterials and their nonlinear interaction with light, there is still an urgent need for highly OL-responsive components. In particular, integrating multiple functionalities into individual nanoscale hybrids with OL response to ultrafast laser pulses is of tremendous importance [11–15]. Compared with the individual constituents, hybrid nanomaterials often exhibit enhanced nonlinear optical (NLO) and OL effects and/or flexible processability, resulting from the unique structures and synergistic coupling effects between the constituents.

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Two-dimensional materials provide a platform for strong light–matter interactions, creating wide-ranging design opportunities via new-material discoveries and new methods for geometrical structuring. Among these, graphene, a nanometer-thick two-dimensional analog of fullerenes and carbon nanotubes, has become one of the most hotly studied of all two-dimensional materials, including widespread research into its optoelectronic applications [16–18]. Furthermore, because its linear band structure allows interbands at all photon energies, graphene has been suggested as a material that might have large third-order $\chi^{(3)}$ nonlinearities. It has been confirmed that graphene nanosheets and their derivatives have excellent third-order NLO and OL performance over a broad wavelength range from the visible to the near infrared region, with versatile optical mechanisms such as saturable absorption (SA), two-photon absorption (TPA) and nonlinear scattering (NLS). These properties give rise to applications in nanophotonic devices, such as mode-lockers, optical limiters, and optical switches [19–23]. Furthermore, graphene and its derivatives, including graphene oxide (GO) and reduced GO (rGO), present two-dimensional structures and readily functionalizable chemistry, allowing them to be combined with complementary NLO materials in tandem configurations, or to be hybridized with other OL components. Therefore, they provide ideal platforms and matrices for constructing graphene hybrids [24–28].

For example, a series of nanoparticle (NP) composites of GO/noble metal (Au, Pt, and Pd) were synthesized via a one-step hydrothermal reaction, and the inclusion of metal NPs on the GO surfaces significantly enhanced the OL properties of GO through NLS effects [24]. Elsewhere, CuO–hydrogen-induced exfoliated graphene nanocomposites showed enhanced OL properties, which arose from the strong nonlinear absorption of semiconducting CuO nanoparticles in the femtosecond (fs) and nanosecond (ns) laser excitation regimes [25]. Both rGO–PbS and graphene–CdS nanohybrids exhibited better OL properties when compared with their naked counterparts upon both 532 and 1064 nm excitation in the ns regime, because of the charge transfer between the two components [26]. The above results strongly suggest that construction of nanohybrids is a facile and effective strategy to improve and tailor the NLO and OL responses of graphene, which consist of a combination of multiple nonlinear mechanisms, including reverse saturable absorption (RSA), TPA, and NLS, as well as photo-induced electron transfer.

Up to now, most studies of the NLO and OL properties of graphene-based nanocomposites have been conducted in solvents. Although liquid matrices allow composite materials to recover quickly from laser irradiation and provide considerable convenience for the study of their properties and mechanisms, they are not suitable for practical applications and device integration. Besides, suspensions of these materials inevitably suffer from agglomeration when deposited for a long period, resulting in deterioration of their NLO and OL properties. To address these problems, the incorporation of graphene-based composites into solid-state matrices could be an effective strategy. Therefore, an important current challenge is to develop methods for stably embedding graphene-based hybrids in an appropriate matrix, or assembling them into solid-state three-dimensional macrostructures, while retaining the inherent properties of the individual OL components. One promising class of solid-state matrices consists of sol–gel-derived, organically modified silicate gel glasses. With good optical transparency, high thermal stability, favorable mechanical characteristics, facile preparation technique, molecular-level uniformity of dopants, and designable microstructures, they represent highly suitable host materials for practical applications, especially in photonics and optoelectronics. Indeed, several research groups have already incorporated graphene into silica gel glasses, and demonstrated the maintenance of the inherent OL effects of graphene [29,30]. However, there has so far been no report of the third-order susceptibility $\chi^{(3)}$ of graphene in solid-state gel glass matrices in the ns regime. Such a discovery would be highly significant to promote the practical and device-compatible development of graphene-based nonlinear photonics.

In the present work, a nanohybrid of ultrafine and well-dispersed carbon quantum dots (CQDs) supported on GO nanosheets was synthesized by a one-step electrochemical method. The nanohybrid was subsequently introduced into organically modified silica gel glasses using the sol–gel wet chemical technique to obtain stable transparent monolithic nanocomposites and explore their practical application in nonlinear optics (Scheme 1). Transmission electron microscope (TEM) and scanning electron microscope (SEM) imaging, Raman spectroscopy, thermogravimetric analysis (TGA), and ultraviolet–visible (UV–vis) spectroscopy were performed to investigate the morphology, structure, and linear optical properties of the CQD/GO $SiO_2$ gel glasses. The NLO properties of the CQD-GO in water and Ormosil gel glass were investigated by the ns open-aperture (OA) and closed-aperture (CA) Z-scan techniques at 532 nm. The results were compared between the water and gel glass phases, and possible mechanisms for the enhancement of NLO behavior of the CQD/GO in the $SiO_2$ gel glass were explored. Meanwhile, the third-order susceptibility of the CQD/GO $SiO_2$ gel glasses was also calculated.

## 2. Experimental

### 2.1. Synthesis

#### 2.1.1. Synthesis of the CQD/GO hybrid nanostructures

The CQD/GO nanocomposites were synthesized by a facile electrochemical method. Typically, a graphite rod (99.99%, Alfa Aesar Co. Ltd.) was inserted into ultrapure water as the anode (18.4 MΩ $cm^{-1}$, 500 mL), which was placed parallel to another graphite rod as the counter-electrode with a separation of 5.0 cm. Static potentials of 30 V were applied to the two electrodes using a direct current (DC) power supply. After continuous stirring for 120 h, the CQD/GO hybrid was obtained, the anode graphite rod became corroded, and a solution appeared gradually in the reactor. The solution was centrifuged to remove the precipitated graphite oxide and graphite particles and filtered and dialyzed with a cellulose ester membrane bag [MD77 (8000–14000)]. The solution was dialyzed and finally concentrated to prepare it for characterization. CQDs were also prepared for comparison purpose.

#### 2.1.2. Synthesis of the CQD/GO $SiO_2$ gel glasses

Optically transparent CQD/GO-doped silica gel glasses were fabricated by hydrolysis and polycondensation of tetraethyloxysilane (TEOS), 3-glycidoxy-propyltrimethoxysilane [$CH_2OCHCH_2O$—$(CH_2)_3$—$Si(OCH_3)_3$, GPTMS], and 3-aminopropyltriethoxysilane [$NH_2(CH_2)_3Si(OC_2H_5)_3$, APTES]. The molar ratio of (TEOS + GPTMS + APTES):ethanol:distilled water in the precursor was 1:4:4, and the molar ratio of TEOS:GPTMS:APTES was 7:2:1. *N*,*N*′-Dimethylformamide (DMF) was introduced as a solvent and drying-control chemical additive at a volume ratio of 0.6 parts DMF per 1 part ethanol. Specifically, 8.0, 2.3, 1.2, 12.1, and 3.7 mL of TEOS, GPTMS, APTES, ethanol, and aqueous CQD/GO, respectively, were mixed under ultrasonication for 30 min. Different amount of the aqueous CQD/GO can result in CQD/GO with different linear transmittance. Subsequently, 7.3 mL of DMF was gradually added to the mixture, which was continuously ultrasonicated for 6 h. The mixture was divided into several parts with equal