



# Preparation, characterization, and nonlinear optical properties of graphene oxide-carboxymethyl cellulose composite films



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## ABSTRACT

The preparation and characterization of free-standing films made of a graphene oxide-carboxymethyl cellulose composite material is described. Characterization was accomplished using transmission electron microscopy, ultraviolet–visible absorption spectroscopy, Raman spectroscopy, and thermal gravimetric analysis. The nonlinear optical performance of this composite material was studied using the open aperture Z-scan technique in the nanosecond regime using a 532-nm wavelength laser. Results show that the composite has nonlinear optical properties that are much enhanced when composited with graphene oxide. All phenomena indicate that the film is a potential candidate for optical limiting applications.

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## 1. Introduction

The optical-limiting (OL) effect is a phenomenon wherein a medium will exhibit high transmittance of a low-intensity light and attenuate an intense optical beam, limiting the output fluence at a certain range. With the extensive use of high-powered lasers in specialized fields such as the military and the healthcare industry, effective optical limiters are crucial for protecting delicate optical instruments, and especially the human eye, from damage caused by intense laser pulses [1–3]. For this reason, many researchers have concentrated on creating ideal OL devices by exploiting OL mechanisms including nonlinear scattering and refraction, and nonlinear absorption processes such as two-photon absorption, multi-photon absorption, free carrier absorption, reverse saturable absorption, and excited-state absorption [4,5]. A combination of two or more of these mechanisms can enhance the OL effect [6–8]. A number of materials have been found to exhibit a strong OL effect and have been explored as candidates for practical optical limiters, including phthalocyanines [9–11], porphyrins [9,12], fullerenes [1], carbon nanotubes [13], nanoparticles [14], metal nanowires [15], and organic chromophores [16].

Graphene is a promising, novel, carbon-based nanomaterial with an atomically thin, two-dimensional structure consisting of sp<sup>2</sup>-hybridized carbon. It exhibits many noteworthy properties, such as a high surface area, superior thermal conductivity, high carrier mobility, and remarkable optical properties [17–22]. Some examples of these remarkable properties are single-atom-thick

graphene displaying hot luminescence and optical transparency by means of nonequilibrium carriers [19]; universal absorbance of single-layer graphene in the near infrared–visible spectral range caused by the linear dispersion of Dirac electrons [21]; and tunable, saturable absorption in the infrared via Pauli blocking [22]. In the past, scientists were devoted to finding a broadband optical limiter for eye protection that covered the entire visible spectrum. However, very few OL materials can fulfill the requirements at all laser pulse lengths. The interband optical transitions in graphene, however, are independent of frequency over a wide range and depend only upon the fine structure constant [21], so it is a promising broadband OL material.

Much work has been done researching the OL property of graphene [23–25] and functionalized graphene [3,26–30]. However, most of the current research investigating the OL effect of graphene is carried out in solution. Although a solution-processed route offers the greatest ease for functionalization and bulk-scale processing, graphitic systems in a liquid phase tend to aggregate into large clusters, which considerably restricts the practical applications of this unique material. Solid-state film structures are more suitable for device applications, so the transfer of the OL properties of graphene from liquid suspensions to solid-state films is very significant. In addition, graphene films are transparent, more flexible, and can be applied in more fields than graphene coating. Therefore, in recent years, researchers have fabricated composite films by incorporating graphene or graphene derivatives into polymer matrices to explore their nonlinear optical (NLO) and OL properties. The reported polymer matrices include sodium salt of poly[2-(3-thienyl)ethoxy-4-butylsulfonate] [31], poly(vinyl acetate) [32], poly(methyl methacrylate) [3,27], bisphenol-A polycarbonate [3], polyvinyl alcohol [33] and so on. After being solidified into a

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film via a polymer, graphene can exhibit its optical properties in practical devices more effectively.

In this paper, we used a quite simple and environmentally benign solution casting method (also named solution mixing- evaporation method) achieved by doping graphene oxide (GO) into a carboxymethyl cellulose (CMC) matrix, thereby producing free-standing composite films [34]. In principle, GO with a tunable energy gap can surpass the NLO properties of graphene, and the good solubility and readily functionalized chemistry of GO allow it to be easily combined with other materials [20]. Besides its role as a film formation agent, the surfactant properties of the CMC eliminate the need to add extra surfactant to the system [35]. Additionally, the long rod-like structure and large dimensions of the CMC may have an OL effect. This work describes the non-covalent incorporation of GO into CMC without disrupting their respective structures to obtain free-standing CMC–GO films. The resulting composites are characterized using a variety of techniques such as transmission electron microscopy (TEM), ultraviolet–visible (UV–vis) absorption spectroscopy, Raman spectroscopy, and thermal gravimetric analysis (TGA). The NLO performance of this composite material is studied using Z-scan measurements.

## 2. Experimental

### 2.1. Film preparation

Graphene oxide was prepared by oxidizing graphite powder in the absence of a sonication step using a modified Hummers method. The graphite powder (5 g) ( $< 45 \mu\text{m}$ , purity  $> 99.99\%$ , USA, Sigma-Aldrich) was mixed with  $\text{H}_2\text{SO}_4$  (110 ml) by stirring, at which point 15 g of  $\text{KMnO}_4$  was slowly added into the suspension. After the reaction was finished, 220 ml of deionized water was added to the resultant purplish-green mixture over a period of 4 h, maintaining a temperature below  $100^\circ\text{C}$ . At this point,  $5\% \text{H}_2\text{O}_2$  was added in drops until the reaction mixture became golden brown. The mixture was then filtered and washed with a  $5\% \text{HCl}$  solution (five times), and then washed repeatedly with distilled water until the pH of the supernatant was neutral and there was no  $\text{SO}_4^{2-}$  in the rinse water. Finally, the material was freeze dried to obtain a loose brown powder.

To prepare three different GO–CMC composite films, we mixed 0.0024/0.0048/0.0074 g GO with 39.52 mL deionized water, and treated them ultrasonically for 1 h to obtain homogeneous and stable GO suspensions. At this point, 0.48 g CMC (degrees of substitution 0.9, 1500–3100 mPa s viscosity, Shanghai, China, Aladdin) was added to the three solutions, fixing the CMC concentration at 1.2 wt% and the original CMC:GO mass ratio at 100:0.5, 100:1, and 100:1.5. Pure CMC solution with the addition of graphene was also made for reference. The four solutions were then mixed thoroughly via ultrasonication (4 h, 100 W) to ensure homogenous mixing, and subsequently ultracentrifuged (acceleration 10,000 rpm, 10 min). The resulting supernatant was removed following ultracentrifugation, and a pure CMC film and three CMC–GO composite films were formed by casting the solution on flat glass substrates and drying the coated films in a vacuum oven at  $50^\circ\text{C}$ . Uniform film thickness was achieved by casting the same amount of film-forming solution on each plate. The final concentration of GO in the films was uncertain and dependent upon the initial concentration in the suspensions. The free-standing films were then able to be peeled from the substrate, and the film thickness was measured to be around 0.03 mm. The film uniformity was carefully checked by optical microscopy and found no observable agglomeration.

### 2.2. Characterization

Transmission electron microscope images of GO were obtained using a JEOL JEM-2010 microscope. To make the SEM samples, the GO was dispersed in water, and a drop of the solution was placed on a copper grid and dried before it was transferred to the TEM sample chamber. Raman spectra were recorded using a Renishaw Invia Raman spectrometer (514.5 nm), and UV–vis absorption spectra were obtained with a Shimadzu UV-2450 spectrophotometer. Thermal properties of the samples were measured using a Q600 SDTTGA/DSC thermogravimetric analyzer under an  $\text{N}_2$  flow rate of 100 mL/min at a heating rate of  $10^\circ\text{C}/\text{min}$ . Unless otherwise specified, all experiments were performed at room temperature.

### 2.3. Nonlinear optical property measurements

The NLO properties of samples were investigated by the Z-scan technique in which a Q-switched Nd:YAG laser (532 nm wavelength) was used as the light source, creating Gaussian pulses of 1 Hz repetition and 8 ns duration. The beam was spatially filtered to remove the higher-order modes, and was focused with a lens at a focal length of 120 mm. The sample was moved along the optical axis (the z-direction) through the focus of the lens. To separate the contributions of nonlinear scattering (NLS) and nonlinear absorption (NLA) of the material, a modified Z-scan system was used. In this case, a detector recorded the reduced transmittance due to NLS and NLA, while another detector measured changes in the scattering solely induced by NLS. The scattered light was collected at  $45^\circ$  to the z-axis. The linear transmittance of the sample was tested at 532 nm using a Shimadzu UV-2450 spectrophotometer. The OL curves, which can be plotted as normalized transmission versus input fluence, were calculated from the open aperture Z-scan data obtained from the samples.

## 3. Results and discussion

Fig. 1(a) shows a typical TEM image of the GO with a sheet-like shape, resembling the waves in a crumpled silk veil. The TEM image indicates that the GO sheets consist of single layers whose size is in excess of several micrometers. The GO shows excellent dispersibility in water, displaying a stable dispersion with a brownish color (Fig. 1(b)). Fig. 1(c) shows a photograph of the four films, and it can be seen that they are uniform and transparent free-standing films.

Fig. 2 illustrates the UV–vis absorption spectra of an aqueous suspension of GO, the pure CMC film, and the three CMC–GO films. The spectrum of GO exhibits two characteristic features that can be used as a means of identification. The first is a maximum ( $\lambda_{\text{max}}$ ) at 227 nm, corresponding to  $\pi \rightarrow \pi^*$  transitions of aromatic C–C bonds; and the second is a shoulder at  $\sim 300$  nm, which can be attributed to  $n \rightarrow \pi^*$  transitions of C=O bonds. The  $\lambda_{\text{max}}$  (227 nm) and the shoulder around 300 nm corresponds to a previous report [36,37]. In the report, the UV  $\lambda_{\text{max}}$  was found to indicate the level of  $\pi$ -conjugation remaining in the system, and thereby the relative degree of oxidation. In this way, a highly conjugated graphene-like material will have a red-shifted  $\lambda_{\text{max}}$ , while material with a disrupted  $\pi$ -network and greater number of  $\text{sp}^3$  carbons will have a blue-shifted  $\lambda_{\text{max}}$ . The more conjugation that is present, the less energy is needed for the electronic transition, which results in a higher  $\lambda_{\text{max}}$  [38]. The  $\lambda_{\text{max}}$  found in this work ( $\sim 227$  nm) indicates the GO we prepared has high oxidation and low conjugation. The spectrum of CMC shows no characteristic absorption peak, and the CMC–GO composites exhibit two shoulders at 227 and 300 nm corresponding to GO, which indicates the successful integration of

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