A photonic crystal based broadband graphene saturable absorber

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The enhanced saturable absorption (SA) of a one-dimensional (1D) photonic crystal (PC) made from polymers and graphene composites by spin-coating is observed. It shows obvious bandgaps at two wavelengths in transmittance. Femtosecond Z-scan measurement at 515 nm and 1030 nm reveals a distinct enhancement in the effective nonlinear absorption coefficient β_{eff} for graphene nanoflakes embedded in the PC, when compared with the bulk graphene-polymer composite. The effect is studied in a wide range of laser intensities. Graphene inclusion into a 1D-PC remarkably decreases the SA-threshold and the saturation intensity, providing a desired solution for an advanced all-optical laser mode-locking device. © 2018 Optical Society of America

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The unique mechanical, thermal, electronic and photonic features of graphene attract much attention. Single two-dimensional graphene layers have a singular structure with K-point linear dispersion relation, zero-bandgap and massless Dirac fermion carriers [1,2]. The difference from bulk graphite crystal induces unusual nonlinear optical (NLO) properties [3,4]. It can generate electron-hole pairs upon laser excitation at any wavelength λ which makes it a progressive solution to ultrafast saturable absorption (SA) [5-8] and optical limiting [9,10]. However, small NLO-coefficient values in natural materials restrict NLO applications to high intensity thresholds. It is understood that embedding NLO materials in a photonic crystal (PC) can yield lower NLO thresholds [11-15].

The 1D-PC is one of the simplest structures. It consists of alternating dielectric materials with different optical refractive indices n . Due to the destructive interferences in such periodic structure, a spectral bandgap (BG) appears in the linear transmission spectrum, meaning that light with a certain λ is reflected by the PC. BG width and depth are determined by the n -difference of materials and by the total number of alternating layers [11]. If the PC embeds high NLO response materials, even weak intensity laser beams change its n -value due to field enhancement inside the structure [12,15], which shifts the BG. Therefore, NLO threshold in a PC can be much smaller than in bulk materials, making it an exciting NLO-device design.

Earlier computer simulation of an embedded graphene-monolayer 1D-PC structure showed SA-threshold decrease by two orders of magnitude for an 818 nm-pump wavelength [16]. We propose a simpler and more accessible technology for PC-manufacturing, based on the polymer dispersion of graphene flakes. We recently experimentally demonstrated the possibility of graphene nanoflakes coated on a mirror to provide intense and fast NLO response with decreased losses for 2 μm -lasers [17]. Developing on this technology, we present a graphene-containing PC designed for IR and visible λ pairs, suitable for the two harmonics of a standard laser source: 1030/515 nm.

To prepare the crystal, graphene was first suspended using the liquid phase exfoliation method [18]. That is, graphite powder was bath-sonicated in a sodium cholate aqueous solution (0.5 wt.%) for 24 h; with 5 g/l graphite concentration. The suspension was then settled for 24 h and its supernatant was taken with a pipette. It was then centrifugated using a ROTOFIX-32A centrifuge for 90 min at 1500 rpm and the supernatant was taken again.

Fig. 1. Characteristics of graphene in aqueous suspension: (a) absorption spectrum in a 1 cm cell; (b) TEM image; (c) Raman spectrum.

The precipitate was filtered using Millipore 0.1 μm filters and weighted in an analytic balance which gave us the graphene concentration of (0.42 ± 0.02) g/l. The absorption spectrum of suspension [Fig. 1(a)] shows the characteristic maximum at 266 nm and cross-section values $\sigma_{\text{Gr}}(1030 \text{ nm}) = (5907 \pm 300) \text{ cm}^2/\text{g}$ and $\sigma_{\text{Gr}}(515 \text{ nm}) = (7600 \pm 400) \text{ cm}^2/\text{g}$. The latter value corresponds to our previous result: $\sigma_{\text{Gr}}(532 \text{ nm}) = 8000 \text{ cm}^2/\text{g}$ [19] for the graphene suspension prepared by tip-sonication. Thin-layer structure of graphene flakes with the transverse sizes of ca. 0.5 – 1.0 μm is seen in Fig. 1(b). The position and shape of 2D mode in the Raman spectrum [Fig. 1(c)] attest the flakes as predominantly monolayer.

We produced the 1D-PCs consisting of 12 alternating layers of poly(9-vinylcarbazole) (PVK) and of graphene-based poly(vinyl-alcohol) (PVA) nanocomposite as schematically shown in Fig. 2(a). The periodic structure was spin coated on a glass substrate. The PVK toluene solution was spin coated for 60 s at 500 rpm and 20 s at 4000 rpm. The graphene suspension mixed in the PVA aqueous solution (PVA-G) was spin coated for 60 s at 500 rpm and 20 s at 6000 rpm. The combination of solvents with contrasted polarity: nonpolar solvent (toluene) for PVK versus polar solvent (water) for PVA-G guaranteed the integrity of each layer during the process. A PC1 sample picture is shown in the Fig. 2(b). The green spot in its center reveals its maximal reflectance in the green. Several concentrations of PVK in the range from ~ 10 to ~ 30 g/l, and those of PVA from ~ 18 to ~ 27 g/l were tried to obtain the structure with appropriate BG positions. The suitable solution was found at $C_{\text{PVK}} = 22.7$ g/l and $C_{\text{PVA}} = 27.3$ g/l. In order to compare the NLO response of graphene in the partially resonant and non-resonant cases, a second PC sample (PC2) and a pure PVA-G film were fabricated by spin-coating with different volumes of the PVA-G solution. Thicknesses of PC1, PC2 and PVA-G are 1732 nm, 2961 nm and 1436 nm respectively, as measured by a Bruker-Dektak stylus-profiler.

Linear light transmission of two samples measured with a PerkinElmer Lambda 750 dual-beam UV-VIS spectrophotometer is shown as solid lines in Fig. 2(c). It is larger than 80% throughout the visible and near-IR in pure PVA-G film. Two BGs near 515 nm and 1030 nm are seen in the PC1 structure. The transmission minimum T_{min} (BG pit) of PC1 is close to 65%. T_{min} of PC2 is about 60%, and its T_{max} (BG top) is lower than that of PC1 owing to its larger thickness and probably light scattering on layer thickness inhomogeneities (LTI). The second BG of PC2 falls on 1425 nm which deprives the possible advantage at $\lambda = 1030$ nm. Spectra of the structures were calculated using the matrix method [20] with a known dispersion $n(\lambda)$ for PVA [21]. That of PVK was numerically obtained by the Lorenz-Lorentz equation through the molecular polarizability a

Fig. 2. (a) Structure of the spin-coated PC; (b) PC1 sample picture, the bar is 1 cm; (c) measured (solid) and calculated (dashed) transmission spectra of PC1 (curve 1), PC2 (curve 2) and PVA-G (curve 3).

calculated by a resonance relation of the Kramers-Kronig type: $a(\omega) = \sum_j f_j / (E_j^2 - \omega^2) + a_0$, where transition energies E_j and oscillator strengths f_j were taken from a PVK absorption spectrum [22] for the first four intensive transitions. Here E_j , ω and a are in atomic units. Static polarizability a_0 was taken to fit $n(589 \text{ nm}) = 1.683$ [23]. Based on the solution-to-solid PVA density ratio, graphene density was expected to be 44 times increased inside the films after drying the liquid coatings. Taking this estimation to the account, the increment due to graphene into the PVA-G refractive index was calculated with the graphene dispersion from [24].

The ratio between PVK and PVA-G layer thicknesses, $L_{\text{PVK}}/L_{\text{PVA-G}}$, within a pair of neighboring layers was varied in a wide range to fit the experimental spectra consistently with the known total thickness of the film. The best coincidences are shown in Fig. 1(b) and correspond to $L_{\text{PVK}}/L_{\text{PVA-G}} = 11/4$ in PC1 and $22/27$ in PC2. The main BG positions coincide and no extra BGs which would appear at other $L_{\text{PVK}}/L_{\text{PVA-G}}$ values are seen. We made certain that the small variations of the polymer refractive index dispersion do not affect the BG position but its depth (contrast). In particular, the calculated shallow pit at the first structure at 1030 nm may be a consequence of insufficiently correct accounting of the graphene increment to $n_{\text{PVA-G}}$. The observed level of the off-resonance transmission in PC-2 structure is apparently due to the scattering on LTI. Nevertheless, the BG positions are found mostly dependent on the $L_{\text{PVK}}/L_{\text{PVA-G}}$ ratio. Therefore, the simulations provide us with realistic values of the layer thicknesses inside the PCs, which are hard to control during the coating procedure.

NLO properties of the three samples were measured by open aperture (OA) Z-scan set up. Laser source was a fiber laser with 340-fs pulse width and 100 Hz-repetition rate. We use a 15 cm focal length lens to focus the laser beam on the sample. The input and transmitted signals were collected by fast silicon detectors. All experiments were performed at the main (1030 nm) and second (515 nm) harmonics. They both perfectly match the two BGs of PC1, but only the second harmonic corresponds to a BG in PC2.

Figures 3(a) and 3(b) show the OAZ-scan normalized transmission curves for PC1, PC2 and PVA-G, obtained at similar input intensities in focus: 3.5, 3.7, 5.1 MW/cm^2 at 515 nm and 2.9, 3.3, 3.4 MW/cm^2 at 1030 nm respectively. All curves show more pronounced SA behavior for the PCs than for the non-crystalline film at both λ . The observed peculiarity of the PC1 structure is its larger bleaching contrast at 1030 nm than at 515 nm (4.7% against 3.6%), that follows the BG depth: more profound in the IR range.

Fig. 3. OAZ-scan results obtained at $\lambda = 515$ nm (a) and 1030 nm (b) and $I_0 \approx 4$ MW/cm² for PC1 (dataset 1), PC2 (dataset 2), PVA-G (dataset 3). Solid lines show fitting results by Eqs. (1), (2).

The SA-contrast of PC2 is inverse: 1.9% at 1030 nm and 3.2% at 515 nm, due to the absence of a BG near 1030 nm. The similar contrast of 0.6% - 0.7% in PVA-G also correlates with the BG absence.

The NLO response was quantified by the effective nonlinear absorption coefficient β_{eff} obtained from fitting the Z-scan curves in Figs. 2(a) and 2(b) according to the well-known formula:

$$T_{\text{Norm}}(z) = \ln \left[\frac{1 + \beta_{\text{eff}} I(z) L_{\text{eff}}}{1 + \beta_{\text{eff}} I(z) L_{\text{eff}}} \right] / \left[\frac{1 + \beta_{\text{eff}} I(z) L_{\text{eff}}}{1 + \beta_{\text{eff}} I(z) L_{\text{eff}}} \right], \quad (1)$$

$$L_{\text{eff}} = \left[1 - \exp(-\alpha_0 L) \right] / \alpha_0,$$

where $I(z)$ is the input intensity with the value I_0 at focus:

$$I(z) = I_0 / \left[1 + (z/z_0)^2 \right], \quad (2)$$

α_0 is the linear absorption coefficient, and z_0 is the Rayleigh length.

To determine SA-thresholds, we recalculated Z coordinates of Fig.3 into the incident laser intensity using Eq. (2), with z_0 obtained from beam waist radii: $z_0 = \pi w_0^2 / \lambda$, $w_0 = 23$ μm (at 515 nm) and 45 μm (at 1030 nm). Then the SA-threshold was found as the intensity where the transmission (the fitting curve as the average property) overgrows 10% of its contrast.

We Z-scanned our samples at different focus intensities: from 10^{-3} to 10 GW/cm², every time evaluating β_{eff} and the corresponding imaginary part of the third-order nonlinear susceptibility: $\text{Im}\chi^{(3)} = (\epsilon_0 \lambda n^2 c \beta_{\text{eff}}) / (3\pi)$, where ϵ_0 is vacuum permittivity. Their absolute values are presented in Figs. 4(a) and 4(b). At high intensities the data points follow the homogeneously broadened (HB) SA model:

$$\alpha_{\text{sat}} = \alpha_0 / (1 + I/I_{\text{sat}}), \quad (3)$$

$$\beta_{\text{eff}} = \alpha_0 / (I_{\text{sat}} + I),$$

represented in the figures by solid curves. A fitting performed with this model provided the saturation intensity, I_{sat} , and the graphene effective linear absorption coefficient, $\alpha_{0,\text{eff}}$. The latter is hardly evaluated based on the transmission spectra because of the mirror structure of the samples. We can see that at low intensities β_{eff} is smaller and the excited states are saturated faster than it is predicted by the model.

Fig. 4. NLO coefficients of PC1 (dataset 1), PC2 (dataset 2) and PVA-G (dataset 3) vs. input intensity at $\lambda = 515$ nm (a) and 1030 nm (b). Solid lines show fitting results by Eq. (3).

It may indicate an influence of other processes which reduce the bleaching, e.g. saturable two-photon absorption (SA-2PA) which has been earlier observed for an epitaxial bilayer graphene [23] and attributed to the carrier-carrier scattering. It can be numerically shown that at an appropriate relation of 2PA coefficient and the 2PA saturation intensity the HBSA-2PA model can fit better the results in Fig. 4. However, the lack of low-intensity data in our case prevents to give an adequate conclusion on the parameters. Therefore, the model (3) with lower number of parameters gives more confident results but neglecting of the said effects.

The SA parameters obtained based on Z-scan fitting by Eq. (1) and $\beta_{\text{eff}}(I_0)$ by Eq. (3) are presented in Table 1. Their values for the bulk film fall within the significant range of variation observed for PVA-G films prepared by different methods [6,25-28]. This indicates a strong dependence of SA on thickness and quality of the graphene sheets as noted in the literature [29]. We can also see that in all aspects SA is several times larger in PCs than in the bulk film at both λ : $\beta_{\text{eff}}^{\text{PC}} / \beta_{\text{eff}}^{\text{film}} \approx 2 - 9$, $I_{\text{thr}}^{\text{film}} / I_{\text{thr}}^{\text{PC}} \approx 1.5 - 3$, $I_{\text{sat}}^{\text{film}} / I_{\text{sat}}^{\text{PC}} \approx 1.4 - 2.7$. The enhanced NLO response is clearly evidenced through an enhancement factor F_{SA} determined as the ratio of PC-to-bulk β_{eff} values. Its values given in Table 1, however, cannot be explained only by the light field enhancement in the PC. The field intensity distributions inside the cavities are calculated by the matrix method together with spectra and the averaged inner intensities I_{film} , are presented in Table 1. We can see that the field enhancement in all the four cases does not differ so much as F_{SA} . However, it explains the small F_{SA} in the case of PVA-G and PC2 at 1030 nm: despite no BG, there's still a residual interference in such structures [12] which enhances the field amplitude inside the films.

Obviously, the SA effect is limited by the bandgap contrast: $\gamma = (1 - T_{\text{min}}) / (1 - T_{\text{max}})$ which is related to the cavity finesse $\mathcal{F} = \pi R / (1 - R)$ [30], where R is the mirror reflectance. The latter can be considered as an analogue of the quality factor for a high-loss interferometer. This is just right for our case, because the low contrast and out-of-resonance transmission (especially in the case of PC2) indicates a high level of loss. At the same time, the classical Q-factor does not consider losses and being obtained from the BG's spectral width, it overestimates the energy accumulated inside the resonator.

Table 1. Saturation parameters obtained from the experimental data fitting, the enhancement factors and the cavity finesse

Structure	β_{eff} cm/MW	I_{lim} kW/cm ²	$\alpha_{0,\text{eff}}$ 1/cm	I_{sat} MW/cm ²	F_{SA}	I_{lim}/I_0	$\mathcal{F}$
515 nm							
PC1	-71.1	4	280	1.6	6.8	1.36	7.9
PC2	-35.2	4	165	1.8	3.4	1.56	3.6
PVA-G	-10.5	10	130	2.6	-	1.06	-
1030 nm							
PC1	-102.0	2	280	1.2	8.2	1.28	8.3
PC2	-20.6	5	110	1.9	1.7	1.17	1.5
PVA-G	-12.4	6	110	3.2	-	1.08	-

Since γ being considered through the Airy function extrema is $(1+R)^2/(1-R)^2$, we can find $\mathcal{F} \approx 2\pi\sqrt{\gamma-1}$. The corresponding finesse values are shown in Table 1 and correlate with the SA enhancement. Here $\mathcal{F}$ of PC2 at 1030 nm is determined through the contrast of the residual interference. Even though $\lambda = 1030$ nm falls on the T_{max} we believe that at high intensity the pattern can be shifted due to a high optical Kerr nonlinearity n_2 of single-layer graphene. For example, $n_2 \sim 1$ cm²/GW of one graphene layer [31] and the effective number of graphene layers in our crystal $N_{\text{eff}} = \alpha_{0,\text{eff}}L_{\text{PVA-G}}/(\sigma_{\text{Gr}}\rho_s)$, where $\rho_s = 77$ ng/cm² is the graphene surface density, give $\Delta\lambda = 2L_{\text{PVA-G}}n_2N_{\text{eff}}I_0 \approx 20$ nm at $I_0 = 3.5$ MW/cm². This effect is less significant in PC1 where $L_{\text{PVA-G}}$ is more than 3 times smaller. The Kerr n_2 also strongly depends on the graphene sheet quality [29], and the evaluation should be considered as a possible circumstance.

In conclusion, we fabricated the 1D-PC with alternating layers of PVA-G and PVK films to enhance the NLO response of graphene. Graphene nanosheets were exfoliated and dispersed in the polymer solution, and the PC was constructed by spin-coating. Periodic structures with two BGs at visible and IR wavelengths were obtained. Significant enhancement of the nonlinear absorption coefficient β_{eff} and the imaginary part of the third-order nonlinear susceptibility $\text{Im}\chi^{(3)}$ was obtained in the PC structures as compared to the bulk PVA-G film. We also showed a remarkable decrease of SA-threshold and saturation intensities of graphene embedded in the PC in comparison with the bulk PVA-G. SA enhancement factor reaches 7 in the visible and 8 in the IR which is explained by the combination of the light field enhancement and absorptive and scattering losses inside the structures. The cavity finesse adequately describes the phenomena. Therefore, a simply spin-coated 1D-PC structure can enhance SA of NLO materials embedded in polymer layers. The combination of graphene, polymer compounds, layer number and thicknesses can be optimized to yield highly effective NLO devices.

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