Graphene and Mo$_2$C vertical heterostructure for femtosecond mode-locked lasers [Invited]

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Abstract: Two-dimensional (2D) materials, which commonly have much higher optical nonlinearity and faster carrier dynamics than their bulk counterparts, hold huge potential for use in nonlinear optical devices, especially in ultrafast mode-locked fiber lasers. Graphene has ultrafast carrier dynamics but the optical absorption is low and the modulation depth is small. It is nontrivial to combine graphene with other 2D materials so as to form a heterostructure with improved optical properties. In particular, recent research has shown that the 2D transition metal carbide (TMC) Mo$_2$C has a very large nonlinear absorption coefficient and can be used as a saturable absorber for mode-locking pulse generation. However, the nonlinear optical properties of the graphene-Mo$_2$C heterostructure have not been investigated. In this work, by directly growing Mo$_2$C nanosheets on the monolayer graphene film and forming the heterostructure, a new kind of saturable absorber was prepared with considerate nonlinear absorption coefficient and large modulation depth. Such a new saturable absorber was evanescently interacted with the side-polished fiber and successfully delivered femtosecond pulse generation at 1550 nm. The combination of two semi-metal 2D materials has enabled the ease of mode locking and stable soliton state pulse generation.

1. Introduction

The study of the nonlinear optical properties of two-dimensional (2D) materials, such as graphene [1–3], black phosphorus (BP) [4,5], transition metal dichalcogenides (TMDs) [6,7], topological insulators (TIs) [8,9], especially their saturable absorption for ultrafast mode-locked lasers has long been a fascinating and exciting research area. Due to the quantum confinement effect, 2D materials commonly have stronger light-matter interaction, larger optical nonlinearity and faster carrier dynamic than their bulk counterpart [10,11]. Therefore, 2D materials with atomic thickness can be directly implemented into the laser cavity as the nonlinear optical device and generate ultrafast mode-locking pulses [11]. Graphene has been intensively studied for the mode-locking pulses generation due to its sub-picosecond level
carrier dynamics and the broadband saturable absorption from 500 nm to over 3000 nm [1,12–14]. However, the optical absorption of graphene is relatively low (2.3% of incident light for monolayer graphene) and its modulation depth is small (<1% for monolayer graphene) [15]. Although the modulation depth can be enhanced by increasing the thickness of graphene, the extra loss will also be induced [16–19]. Recently, other 2D materials such as BP, TMDs, TIs, were also employed as the saturable absorbers and demonstrated in pulse laser applications [20–24]. For example, 3-4 layered BP has direct bandgap at 0.8 eV, which provide it a large optical absorption at the 1550 nm, so it is very suitable for ultrafast pulsed lasers at telecommunication wavelength. But the material is not stable at the ambient environment and careful encapsulation is essential [4,5,23]. 2D TMDs (e.g., MoS2, WS2, MoSe2, and so on) have large nonlinear absorption coefficient compared to graphene (~250 cm/GW) [25] and their bandgaps are commonly around 1.6 eV to 2.5 eV [26], making them suitable for visible photonic applications [27]. TIs have small bandgaps (~0.3 eV in Bi2Te3) [28], which indicate that they are suitable for broadband operation of mode-locked lasers [9,28].

2D transition metal carbides (TMCs), known as MXenes materials with a general structure $\text{M}_{n+1}\text{X}_n\text{T}_x$ (M is early transition metal such as Mo and Ti, X represents Carbon or nitrogen and T is the surface terminations), are recently discovered as the new members of 2D materials [29,30]. They have high conductivity, tunable bandgap range from metallic to semiconductor, excellent mechanic properties, therefore, MXenes are considered as a promising materials for energy storage [31] and superconductivity applications [32]. Recently, Mo2C as a typical MXenes material was discovered to have a very high nonlinear absorption coefficient (~10^5 cm/GW) and realized both 1 and 1.5 µm mode-locked fiber laser output. The pulse duration were 418 ps and 1.28 ps, respectively [33]. Since both graphene and Mo2C are semi-metals with ultrafast carrier dynamics and has similar lattices constant, it is interesting to study the nonlinear optical properties or laser performance of graphene/Mo2C heterostructure.

In this work, Mo2C nanosheets were directly grown onto a monolayer graphene film by chemical vapour deposition (CVD) method. The graphene-Mo2C heterostructure shows a considerable nonlinear absorption coefficient and a large modulation depth. By simply tiling the heterostructure film onto the side-polished fiber and insert into a 1.5 µm fiber laser cavity, ultra-short soliton pulses with 723 fs were generated. The mode-locked fiber laser could continually run over 5 hours with high power and spectrum stability. Our work provides a simple saturable absorber based on graphene-Mo2C heterostructure and indicate the promising potential of TMCs and 2D materials in photonic applications.

2. Results and discussion

The graphene-Mo2C heterojunction materials were obtained by CVD production, where the fabrication method was similar to the previous paper [34]. A Cu foil as the substrate was tiled on a Mo foil. When the temperature was increased to 1070 °C, H2/Ar and CH4 was introduced for growing graphene on the Cu surface. Then the temperature was continually increased to 1090 °C. Cu foil would melt and Mo atoms would raise to the Cu surface and contacted with CH4. Through controlling other parameters such as gas flow, Mo2C nanosheets with high quality were grown underneath the graphene on the melted Cu substrate. For the ease of our materials characterization and photonic application, Cu substrates was etched by (NH4)S2O8 solution with the concentration of 0.2 M and the graphene-Mo2C samples was transferred onto SiO2, quartz and side-polished fiber substrate. During the etching process, due to the isolation of graphene layer, Mo2C nanosheets were protected and no any damage by the etching solution. Figure 1(a) shows the optical image of the sample on the SiO2 substrate. It is clear that Mo2C nanocrystals with regular shapes are randomly distributed on the graphene film. The surface of the Mo2C nanocrystal are uniform, which was further investigated by the atomic force microscopy (AFM) measurement as shown in Fig. 1(b). The thickness of the
The nanocrystal is around 7.8 nm. Figure 1(c) is the optical image that the sample was transferred onto the intersecting surface of the side-polished fiber. We can see the flexible heterostructure film were attached to the fiber well. Due to the limit of the resolution of our optical microscopy and the influence of the height of the fiber, more image with higher resolution was hardly obtained. The morphology of the single Mo2C nanocrystal was shown in the transmission electron microscopy (TEM) image in Fig. 1(d). The side length of the hexagonal Mo2C nanocrystal is around 600 nm. In the corresponding high-resolution TEM image as shown in Fig. 1(e), the configuration of Mo and C atoms are tidy and no defect was observed, indicating the good crystal quality of Mo2C. The selected area electron diffraction (SAED) was also employed for the crystal characterization of the heterostructure sample. It is interesting that two sets of hexagonal diffraction patterns are observed in the image of Fig. 1(f). They are in response to the monolayer graphene layer (marked by the green dots) and the Mo2C nanocrystals (marked by the red dots). It should be noted that the 6-fold diffraction patterns have nearly the same orientations, which indicate that graphene [35] and Mo2C [36] have little lattice mismatch and their heterojunction was formed.

In order to further study the interaction between graphene and Mo2C, the Raman spectrum of pure graphene, Mo2C and the heterostructure samples were compared in Fig. 2(a). Compared with their positions in pure graphene, the G and 2D peak of graphene in the heterostructure sample have blue-shift around 10 cm$^{-1}$ (1590.4 cm$^{-1}$ to 1600.7 cm$^{-1}$) and 40 cm$^{-1}$ (2681.2 cm$^{-1}$ to 2720.8 cm$^{-1}$), respectively. Meanwhile, the characteristic Raman peak in Mo2C was shifted from 142.6 cm$^{-1}$ to 148.7 cm$^{-1}$. While in previous reports about the stack structure of graphene and other materials, their G and 2D peak have no shift with that of original graphene [37]. The peak shift in the Raman spectra indicates the weak surface interaction between the two components in the heterostructure.
The optical absorption spectra of graphene, Mo$_2$C and the heterostructure samples were also measured as shown in Fig. 2(b). Graphene as a typical dirac material has flat optical spectrum in visible and infra waveband. Mo$_2$C is a conductor material without bandgap [30] and a strong and flat optical absorption curve is measured as the blue line in the Figure. The graphene/Mo$_2$C sample obviously inherits the wideband optical response characteristics of original graphene and Mo$_2$C and the absorption capability is even better than Mo$_2$C.

![Fig. 2. Raman spectra (a) and optical absorption spectra (b) of graphene (Red line), Mo$_2$C (Blue line) and their heterostructure sample (Black line).](image)

The open-aperture Z-scan setup at the wavelength of 1064 nm was performed for measuring the nonlinear optical absorption response of the heterostructure sample on the quartz substrate. A Ti: Sapphire regenerative amplifier system was employed as the light resource with the pulse duration of 45 fs and the repetition rate of 2 kHz. The incident light was split by a 95/5 spectroscope. The main light path illuminated the sample which was fixed on the motorized linear translation stage by a focused lens with the work distance of 150 mm, and then monitored by a detector. The other light path was as the reference light and received by another detector. By varying the distance between the sample and the lens, the incident light intensity on the sample would be changed and the intensity-dependent transmission curve would be obtained. Figure 3(a) is the measured Z-scan curve at the incident light intensity of 7.99 GW/cm$^2$. The normalized transmittance increases rapidly when the sample position is closed to the lens focus ($Z = 0$), which shows the typical saturable absorption phenomenon. The measured data can be fitted by the following formulation:

$$T_{\Delta\ell}(z) = \frac{1}{\sqrt{\pi q_0}} \int [\ln(L + q_0 e^{-x^2})] dx$$

Here, $q_0 = \beta I_0 L_{\text{eff}}$, $\beta$ is material’s nonlinear absorption coefficient, $I_0$ is incident Intensity at the focus, $L_{\text{eff}}$ is related to the sample’s path length. Through the fitting curve, the $\beta$ value of the sample is calculated to 5.07 cm/GW, which is similar to that of graphene [15] and indicate the huge nonlinear absorption capability of the heterostructure.
Fig. 3. Z-scan spectrum (a) of the Mo₂C-graphene hetero-structure sample and its corresponding saturable absorption spectrum (b).

The light intensity distribution along the Z position can be transformed by the formulation
\[ I = I_o \left(1 + \frac{Z^2}{\left(\frac{\pi w_0}{\lambda}\right)^2}\right) \]  
\( w_0 \) is the waist radius of the light at lens focus. The saturable absorption characteristics can be obtained as shown in Fig. 3(b). By the Fitting formulation:

\[ T = \left(1 - \frac{\alpha_s}{I} - \beta I L\right) \left(1 - \alpha_s\right) \]  
(2)

Here, the modulation depth \( \alpha_s \), which is defined as the whole change of absorption by increasing the incident light power from low intensity to saturable intensity, is highly at 55.6%. And the saturable intensity, which is defined as the required optical intensity to the half of its unbleached value, is calculated to 58.51 GW/cm². The relatively large saturable intensity may because that the incident pulse duration is very short [19]. The large modulation depth indicates that the heterostructure saturable absorber can generate mode-locking pulses with ultra-short duration.

Table 1. Comparisons of nonlinear optical absorption of graphene, Mo₂C and their heterostructure

<table>
<thead>
<tr>
<th>Material</th>
<th>Measurement wavelength (nm)</th>
<th>Nonlinear absorption coefficient ( \beta ) (cm/GW)</th>
<th>Saturable intensity ( I_s ) (GW/cm²)</th>
<th>Modulation depth (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolayer Graphene</td>
<td>1550</td>
<td>-100</td>
<td>&lt;0.06</td>
<td>&lt;1.5</td>
<td>[15][18]</td>
</tr>
<tr>
<td>Mo₂C (Thickness ~15 nm)</td>
<td>1550</td>
<td>-9 x 103</td>
<td>0.18</td>
<td>8.6</td>
<td>[33]</td>
</tr>
<tr>
<td>Graphene/Mo₂C (Thickness of Mo₂C~7.5 nm)</td>
<td>1550</td>
<td>-5.07</td>
<td>58.51</td>
<td>55.56</td>
<td>This work</td>
</tr>
</tbody>
</table>

As discussed above in Table 1, the graphene/Mo₂C heterostructure sample was etched the Cu substrate and transferred onto the side-polish fiber as the in-line saturable absorber. The laser cavity is as shown in Fig. 4. A 980 nm laser diode as the pump incidented into the cavity by a 980 nm/ 1550 nm wavelength division multiplexer (WDM). The gain medium was a piece of Er-doped fiber (EDF) with 3 m length. The absorption coefficient of EDF is 80 dB/m. The isolator ensured the right circulation direction of the intra-cavity light and the 10% coupler was employed as the laser output. Before inserting the saturable absorber into the cavity, no any mode-locking phenomenon was observed even though different intra-cavity
polarization was adjusted, in which the self-mode-locking behaviour was excluded. Then the graphene/Mo$_2$C saturable absorber was inserted between the coupler and the polarization controller (PC) as the evanescent interaction with the intra-cavity light. Firstly, the output state is continuous wave state, the output power has no obvious change during this process, indicating that the polarization-dependent loss of the saturable absorber is little. The mode-locking operation would occur under a suitable polarization state and the output power is smaller than the continuous wave output state.

![Fig. 4. Laser cavity schematic. LD: 980 nm laser diode; WDM: wavelength division multiplexer; EDF: Er-doped fiber; ISO: Isolator; PC: Polarization controller.](image)

By optimizing the cavity parameters, the stable soliton mode-locking output of the 1.5 µm graphene/Mo$_2$C fiber laser was obtained as shown in Fig. 5. The optical spectrum under the pump power of 326 nm is in Fig. 5(a). The center wavelength is 1599 nm and the 3dB bandwidth 4.1 nm. Symmetry and sharp Kelly sideband can be observed, which indicates that the laser is working on the conventional soliton state. The pulse train is quite stable without modulation wave on the top of the pulse (Fig. 5(b)). The pulse repetition rate is 15.33 MHz and the corresponding time interval is 65.2 ns, which is matched well with the cavity length of 13.04 m. By the monitor of an autocorrelator, the single pulse envelope is obtained in Fig. 5(c), with the pulse duration shortly at 723 fs. The time-bandwidth product is calculated to 0.348, which is very close to that of idea sech$^2$ pulses, indicating little chirp of the mode-locking pulses. For further studying the pulses stability, the radio-frequency (RF) spectrum is obtained in Fig. 5(d). The signal-noise rate of the fundamental frequency is highly at 68.6 dB, informing that the soliton output has very high quality. Furthermore, the high-order frequency is also stable up to 500 MHz range.

It is interesting that when the pump power is continually increased to the maximum power value (850 mW), the fundamental soliton mode-locking state is still stable, without any other soliton phenomenon happening such as pulse splitting or harmonic soliton mode-locking. The main reason is that the heterostructure sample was transferred onto the side-polish fiber and evanescent field interacted with the intra-cavity light. In this way, the modulation length of the sample would be longer and the thermal damage threshold of the saturable absorber device would be raised. In the other way, because of the long modulation distance, the output power is relatively low and the pulse split phenomenon is suppressed. The relationship between the pump power and the output power is shown in Fig. 5(e). The maximum output power is 10.93 mW, which corresponds the maximum pulse energy and the highest peak power are 0.713 nJ and 986.14 W, respectively, indicates the new type of saturable absorber has application potential in high-energy lasers.

The long-term stability performance of mode-locked fiber lasers under the ambient environment is permanent for the practical application. Here, the output characteristics of our graphene-Mo$_2$C mode-locked fiber laser was continuously monitored over 5 hours and the optical spectra was recorded every 1 h. During the measurement period, the vary range of the
center wavelength in the optical spectra was between 1599.297 nm to 1599.352 nm and the 3 dB bandwidth varies from 4.031 nm to 4.096 nm. The variation of the optical spectra is less than 2%, which indicate the high stability of the laser device.

![Image](image_url)

Fig. 5. The mode-locked fiber laser based on the Mo2C-graphene hetero-structure saturable absorber. (a) Optical spectrum. (b) Pulse trains. (c) Autocorrelation curve of the single mode-locking pulse. (d) Radio-frequency (RF) spectrum. (e) Output power with the increase of input power. (f) long-stability measurement of the laser optical spectrum.

3. Conclusion

In conclusion, the graphene-Mo2C heterostructure was demonstrated as a new kind of saturable absorber, which has large nonlinear absorption coefficient of 5.07 cm/GW and modulation depth of 55.6%. By inserting the saturable absorber into the 1.5 µm fiber laser and forming evanescent interaction with the intra-cavity light, the soliton mode-locking pulses with 723 fs pulse duration would be generated. Even the pump power is continuously increased to the maximum power value (850 mW), the fundamental soliton mode-locking state is still stable, without any other soliton phenomenon happening such as pulse splitting or harmonic soliton mode-locking. Furthermore, the optical spectra variation is less than 2% during running the fiber laser over 5 hours. Our work indicates graphene-Mo2C heterostructure is promising for nonlinear optical applications.

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