Front. Optoelectron. 2016, 9(2): 259–269
DOI 10.1007/s12200-016-0618-z

REVIEW ARTICLE

Progress on mid-IR graphene photonics and biochemical applications

Zhenzhou CHENG (✉)[1], Changyuan QIN[1], Fengqiu WANG (✉)[2], Hao HE[3], Keisuke GODA (✉)[1,4,5]

1 Department of Chemistry, University of Tokyo, Tokyo 113-0033, Japan
2 School of Electronic Science and Engineering, Nanjing University, Nanjing 210023, China
3 Med-X Research Institute, School of Biomedical Engineering, Shanghai Jiao Tong University, Shanghai 200031, China
4 Department of Electrical Engineering, University of California, Los Angeles 90095, USA
5 Japan Science and Technology Agency, Tokyo 102-0076, Japan

Abstract Mid-infrared (mid-IR) (2 – 20 μm) photonics has numerous chemical and biologic "fingerprint" sensing applications due to characteristic vibrational transitions of molecules in the mid-IR spectral region. Unfortunately, compared to visible light and telecommunication band wavelengths, photonic devices and applications have been difficult to develop at mid-IR wavelengths because of the intrinsic limitation of conventional materials. Breaking a new ground in the mid-IR science and technology calls for revolutionary materials. Graphene, a single atom layer of carbon arranged in a honey-comb lattice, has various promising optical and electrical properties because of its linear dispersion band structure and zero band gap features. In this review article, we discuss recent research developments on mid-IR graphene photonics, in particular ultrafast lasers and photodetectors. Graphene-photonics-based biochemical applications, such as plasmonic sensing, photodynamic therapy, and florescence imaging are also reviewed.

Keywords mid-infrared (mid-IR), graphene, lasers, photodetectors, optical sensing and sensors, photodynamic therapy, spectroscopy, fluorescence and luminescence

1 Introduction

The mid-infrared (mid-IR) spectral region (2 – 20 μm) is attractive for a broad range of basic science, industry, energy, and medicine. In this region, many important molecules undergo strong and distinctive fundamental vibrational and rotational transitions, such that mid-IR absorption lines are about three orders of magnitude larger than overtones situated in the visible light or near-IR wavelengths [1]. The mid-IR spectroscopy provides a powerful tool for nonintrusive measurement and biochemical structure analysis. For example, the large absorption cross-section renders detection of trace gases at the parts-per-billion (ppb) and parts-per-trillion (ppt) levels, which is of great interest in a wide range of studies such as breath analysis for disease diagnosis, greenhouse gas monitoring, and toxic vapor detection. In biologic applications, the "fingerprint" absorption characteristics enable the possibility of tracing out the biologic sample's chemical and physical information, which can be used for disease diagnosis, drug development, and biologic imaging. Ultrafast lasers and highly sensitive photodetectors are critical components in mid-IR photonics, but have been challenging to develop. Despite rapid technological advancements with mid-IR gain materials [2], the lack of a high-performance saturable absorber, or a passive ultrafast optical switch, significantly limits the development of convenient mid-IR ultrafast lasers. One limitation comes from the difficulty of band gap engineering and growth techniques of conventional materials. For example, the traditional semiconductor saturable absorption mirror (SESAM), a nonlinear device used in passive mode-lock technology, is expensive and only suitable for a specified wavelength (below 2 μm) with a bandwidth of tens of nanometers [3]. State-of-the-art mid-IR detectors normally use low band gap semiconductors such as HgCdTe alloys or quantum structures on III-V materials [4], which are difficult to operate at room temperature. Thus, the mid-IR photonic system often suffers from high cost, bulky setup, and complex operation. A breakthrough in mid-IR science and technology will require revolutionary materials.

Graphene is a two-dimensional (2D) material that has

Received February 1, 2016; accepted February 17, 2016

E-mails: zzcheng@chem.s.u-tokyo.ac.jp, fwang@nju.edu.cn, goda@chem.s.u-tokyo.ac.jp

one single layer of carbon atoms arranged in a honey-comb lattice [5] and is a promising material to overcome the technical challenges for investigating the mid-infrared photonic functionalities [6,7]. Although the hexagonal lattice of carbon atoms has been found in the quasi-0D (fullerenes), quasi-1D (carbon nanotubes), and 3D (graphite) allotropes of carbon, graphene possesses unique electronic and optical properties which are different from other allotropes. Because of the linear energy dispersion relation, graphene exhibits a wavelength-independent saturable absorption, spanning from the visible light to mid-IR wavelengths. This cannot be satisfied by single-wall carbon nanotubes (SWNTs), where the working wavelength is determined by the diameter and the working bandwidth is only ~100 nm [3]. For graphene, the carrier recombination is typically an order of magnitude faster than that of SWNTs [8,9]. Although there were initial doubts that too fast recombination rate may lead to insufficient saturable absorption, early experimental works nevertheless demonstrated good nonlinear absorption characteristics of graphene at the telecommunication wavelengths [10–12]. Graphene is a zero energy band gap material in which electrons behave like massless Dirac fermions with ultrahigh carrier mobility (up to 15000 $cm^2/V/s$). Graphene photodetectors have a potential ultrahigh working bandwidth (up to 500 GHz), with the spectral region covering from the visible light to terahertz frequencies [13]. Moreover, graphene, as a type of group IV material, shows great potential for the complementary metal-oxide semiconductor (CMOS) compatible process. This process offers the advantages of low-cost, high-volume, and reliable manufacturing.

Graphene has stimulated tremendous research interests in plasmonics–coherent electron oscillations that normally exist at the interface between metals and dielectrics. Graphene poorly demonstrates plasmonic effects at the visible light and near-IR wavelengths, but mid-IR plasmonics is feasible [14]. Low carrier concentration opens opportunities for tunable carrier density by means of electrostatic doping or chemical doping, which is impossible to achieve in traditional noble materials, such as Au and Ag. Alternatively, nanostructures on graphene, such as nanoribbons or nanodisks, can help demonstrate localized mid-IR plasmonic devices [15]. Graphene thus provides a great platform for low-loss and tunable mid-IR plasmonic applications. Furthermore, based on its unique chemical and physical properties [16–19], graphene and graphene-based nanomaterials have attracted strong interests from biologists. Specifically, the discovery of the adsorption of single-stranded DNA (ssDNA) onto graphene sheets, the ability of graphene to quench electron donors, the ability of graphene to protect biomolecules from enzymatic cleavage, as well as transportation capability in living cells and *in vivo* systems have revealed the potential for graphene applications in biology and biochemistry. Thereby, a series of new methods have been developed for biofunctionalization with biomolecules using graphene.

In this review article, we discuss the latest status about the development of mid-IR graphene photonics and biochemical applications. Specifically, in Section 2, we discuss research progress on mid-IR ultrafast lasers by using graphene as a saturable absorber. In Section 3, we explain the working principles of different types of photodetectors and review previous efforts on the development of mid-IR graphene photodetectors. In Section 4, we discuss various biochemical applications including mid-IR plasmonic sensing, photodynamic therapy, and florescence imaging. In Section 5, we discuss the further perspective of mid-IR photonics with graphene and other 2D materials. In Section 6, we summarize this article.

2 Ultrafast lasers

In this section, we introduce the use of monolayer graphene as a saturable absorber in a passive mode-locked mid-IR laser. Specifically, we discuss recent experimental demonstrations of ultrashort pulse generation at mid-IR wavelengths in fiber lasers and solid-state lasers.

The exploration of graphene-based mid-IR pulsed lasers started in 2012, with several groups reporting developments around 2 μm. Typical saturable absorbers were in the form of either graphene-polymer composite films or chemical-vapor deposition (CVD) grown graphene followed by transferring to metal or dielectric mirrors. For fiber lasers, liquid exfoliated graphene-based composite films were first used to demonstrate a *Q*-switched laser [20] and a mode-locked thulium fiber laser [21], respectively. The use of composite films ensures higher absorption and larger modulation depth, which is desirable for pulsed operation in fiber lasers. On the other hand, single-layer CVD graphene-based saturable absorber mirror has the advantages of high transmittance (~ 97%) and controllable and scalable fabrication. The relatively smaller modulation depth (typically below 1%) of single-layer graphene makes it a good alternative to the widely used SESAMs. The first CVD graphene enabled mode-locked solid-state crystal laser was based on a Tm-doped calcium lithium niobium gallium garnet (Tm:CLNGG) gain media, where the generation of 60 mW, 729 fs pulses at a wavelength of 2018 nm was achieved [22]. Graphene was transferred onto a dielectric mirror and the device was operated in the reflectance mode as a cavity end mirror [22]. By transferring graphene to a transparent dielectric substrate, a Tm:Lu_2O_3 crystal laser was mode-locked in such a way that shorter (~ 410 fs) and more powerful (~270 mW) pulses were obtained [23]. Thus far, the longest wavelength graphene enabled mode-locked solid-state laser is based on a Cr: ZnSe laser, operating at 2500 nm, in which graphene transferred onto a CaF_2 substrate acted as an

absorber in the transmission mode [24]. The laser features a further reduced pulse duration of 226 fs, with 80 mW output power. Graphene-based saturable absorber devices can take other forms such as those directly deposited on SiC substrates. *Q*-switched operation of a Tm:YAG laser was demonstrated using such a device [25], but the use of such devices is not widely applicable to fiber lasers.

It should be mentioned that in the 2 μm wavelength region, more conventional methods such as those based on carbon nanotubes and SESAMs also work quite effectively. For example, SWNTs were used to mode-lock a solid-state lasers at a wavelength of 2.35 μm [26]. The real comparative advantage of graphene lies in its scalability further into the mid-IR range. Wei and coworkers demonstrated the first graphene-based pulsed laser operation at a wavelength close to 3 μm, where graphene was deposited onto a fiber ferrule mirror using the optically driven deposition method [27]. The laser emitted 2.9 μs pulses with a pulse energy up to 1.67 μJ. By optimizing the fiber laser cavity and using a multi-layer graphene covered gold mirror, as shown in Fig. 1, the same group of researchers reported mode-locked operation at a wavelength of 2.8 μm with a pulse duration ~ 42 ps [28]. This is the longest laser wavelength at which graphene-based passive mode-locking has been demonstrated to date. The performance of mid-IR graphene mode-locked lasers is shown in Table 1.

3 Photodetectors

In this section, we discuss different working mechanisms of graphene photodetectors, including the photovoltaic effect, photoconductive effect, photothermoelectric effect, and bolometric effect, as shown in Fig. 2. Specifically, we introduce experimental demonstrations of various types of mid-IR photodetectors, based on graphene and hybrid architectures, which are realized by combining graphene with other structures or materials.

For the photovoltaic effect, electrons present in the valence band, being excited by incident photons, jump to the conduction band and become free, as shown in Fig. 2 (a). Photoexcited electron-hole pairs are then separated by the internal electrical field at the graphene p-n junction.

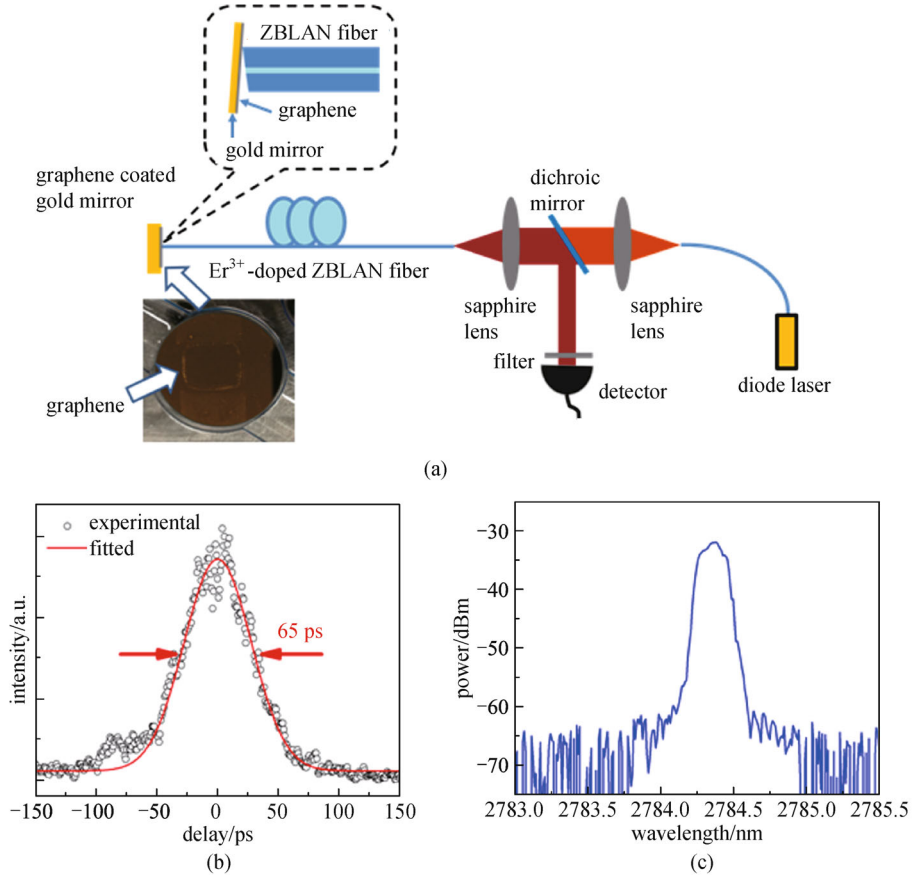


Fig. 1 Graphene-based mode-locked pulse laser [28]. (a) Er^{3+}-doped ZrF_4-BaF_2-LaF_3-AlF_3-NaF (ZBLAN) fiber laser incorporating a multi-layer graphene mirror as a saturable absorber; (b) measured autocorrelation trace showing a full width at half maximum (FWHM) pulse width of 65 ps. Assuming a $sech^2$ profile, this yields a pulse duration of ~ 42 ps; (c) optical spectrum of the mode-locked laser, showing a mid-IR center wavelength of ~2.78 μm

Table 1 Performance of mid-IR graphene ultrafast lasers

reference	gain medium	pulse width	peak power	center wavelength
Wang et al. [20]	Tm-doped fiber	2.3 μs	30 mW	1884 nm
Zhang et al. [21]	Tm-doped fiber	3.6 ps	111 W	1940 nm
Ma et al. [22]	Tm:CLNGG crystal	729 fs	837 W	2018 nm
Lagatsky et al. [23]	Tm:Lu_2O_3 crystal	410 fs	5.99 KW	2067 nm
Cizmeciyan et al. [24]	Cr:ZnSe cyrstal	226 fs	4.60 KW	2500 nm
Wang et al. [25]	Tm:YAG crystal	2.25 μs	690 mW	2010 nm
Tolstik et al. [26]	Cr:ZnS crystal	61 fs	62.30 KW	2350 nm
Wei et al. [27]	Er^{3+}-doped ZBLAN fiber	2.9 μs	580 mW	2783 nm
Zhu et al. [28]	Er^{3+}-doped ZBLAN fiber	42 ps	16.67 W	2784 nm

The built-in electrical field in graphene is formed by the electrostatic doping, or by using contact materials with different work functions, which can dope graphene beneath n-type or p-type. Mueller et al. utilized inter-digitated metal fingers of different metals to enlarge the built-in electrical field as well as increase the light-detection region in graphene. They demonstrated a 10-GHz graphene photodetector at the wavelength of 1.55 μm. The potential spectral band of the photodetector can be expanded to the wavelength of 6 μm [29]. In our previous work, we integrated graphene on a silicon suspended membrane waveguide [30] and silicon-on-sapphire (SOS) waveguide [31] to increase the graphene absorption by using the evanescent field coupling, as shown in Figs. 3 and 4. The built-in electrical field at the graphene/silicon heterostructure enables a high-responsivity photodetection under the 2.75 μm wavelength light excitation.

For the photoconductive effect, as shown in Fig. 2(b), photo-excited carriers alter the conductance of graphene by $\Delta\sigma \propto \mu \cdot \Delta n$, where μ is the carrier mobility and Δn is the photo-excited change of carrier density, which scales linearly with the carrier lifetime. Compared to the photovoltaic detector, graphene photoconductors normally have a higher responsivity, but lower dynamic response, since the responsivity is improved by increasing the photo-excited carrier lifetime. Liu et al. proposed and demonstrated a mid-IR photodetector with a double-layer graphene sandwiching a thin tunnel barrier structure [32].

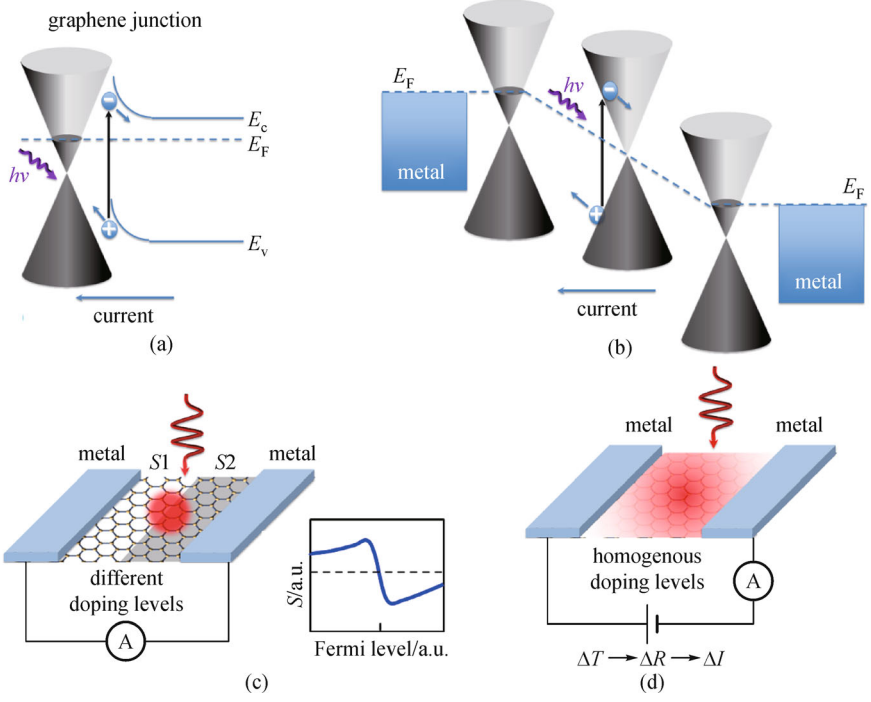


Fig. 2 Schematic pictures showing different working mechanisms of graphene photodetectors. (a) Photovoltaic effect; (b) photoconductive effect; (c) photothermoelectric effect; (d) bolometric effect

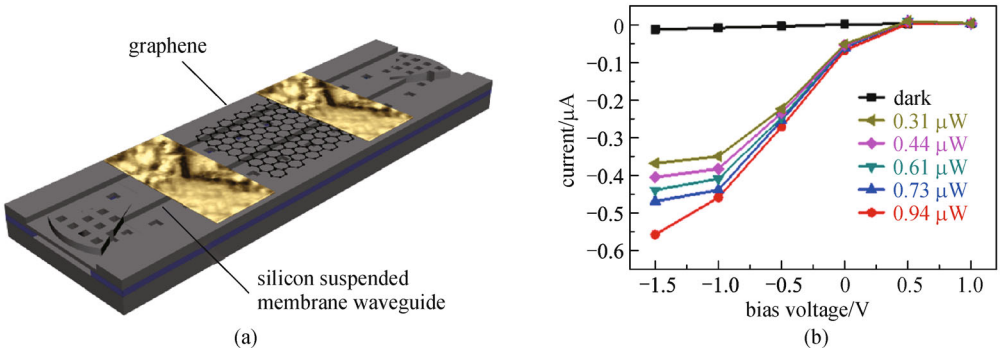


Fig. 3 Graphene on a silicon suspended waveguide as a photodetector [30]. (a) Schematic picture of the graphene photodetector; (b) dark current and photocurrent measurements under different bias voltages at the wavelength of 2.75 μm

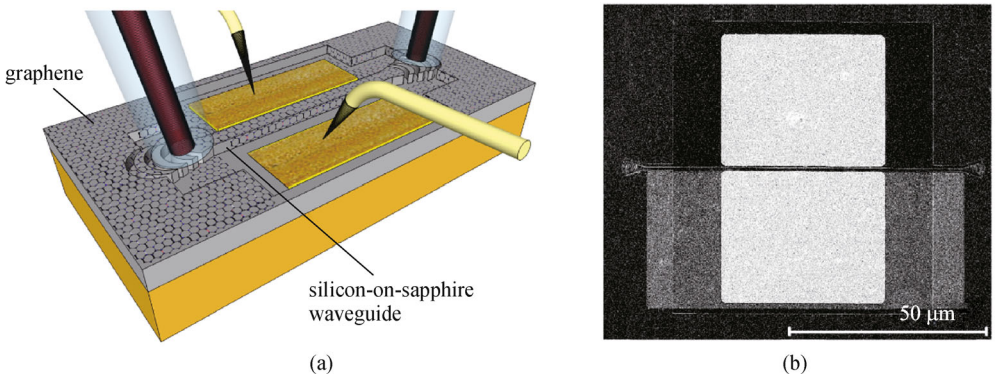


Fig. 4 Silicon-on-sapphire (SOS) waveguide photodetector [31]. (a) Schematic pictures of the photodetector; (b) scanning electron microscope image of the photodetector. The patterned region (without graphene) shows a clear contrast

Under light illumination, the top layer graphene acts as a gate and introduces an electrical field to the bottom graphene layer. This structure prolongs the recombination time of photo-excited carriers and achieves a high responsivity in the mid-IR spectral region. Zhang et al. introduced electron trapping centers and a band gap to the graphene by fabricating the quantum dot-like structure, which helps increase the carrier lifetime and enhance the photoresponse [33]. In another piece of work, the metallic antenna was used to enhance the graphene absorption and improve the responsivity of photodetectors at the mid-IR resonant frequency [34]. The antenna rods also acted as nanoelectrodes, providing enhancement of photocarrier collection.

For the photothermoelectric effect, the incident light generates a temperature gradient at the graphene interface junction where doping levels of two sides are different, and finally results in a thermoelectric voltage $(S1-S2)\cdot\Delta T$, where $S1$ and $S2$ are Seebeck coefficients in different doping regions and ΔT is the electronic temperature difference between the different doping sides of graphene, as shown in Fig. 2(c). The device is operated under the zero-bias condition, which is promising for the low dark-current. The sign of the photothermoelectric current is opposite to the photovoltaic current in the graphene bipolar p-n junction and the unipolar p^+-p or n-n^- junction. Hsu et al. demonstrated a graphene-based thermal imaging system by integrating graphene photothermoelectric detectors with silicon nitride membranes at the wavelength of 10.6 μm [35]. Badioli et al. observed an enhanced photothermoelectric photoresponse under the mid-IR light excitation [36] since mid-IR light can provide an efficient way to excite bulk or surface phonons, which can in turn locally heat up graphene charge carriers.

For the bolometric effect, the light illumination produces heat and results in a change of the resistance of the graphene device, as shown in Fig. 2(d). Since the resistance change should be converted to a detectable electrical signal, it often requires an external bias and is operated in homogenous highly doped graphene without the need of the p-n junction structure. This type of thermal detector provides a high sensitivity and does not require cryogenic cooling to mitigate noise. Unlike the photoconductive effect, in which photo-excited carriers increase the carrier density and enhance the device conductance, the photo-induced temperature increase will reduce the carrier mobility and reduce the conductance. In our former studies, we have demonstrated a highly p-type doped

graphene photodetector integrated on the silicon nitride waveguide to enhance the absorption at 1.55 μm wavelengths [37]. The spectral bandwidth of the proposed device can cover the transparent window of silicon nitride material (up to 5.5 μm). Yan et al. demonstrated the graphene bolometer with a due-gate configuration which creates a tunable bandgap and electron-temperature-dependent conductivity in the bilayer graphene [38]. The bolometer exhibits a low noise-equivalent power, and a high intrinsic speed. Freitag et al. also report the mid-IR bolometric photocurrent measurement in graphene nanoribbon arrays on SiO_2 substrate [39], where a strong coupling exits between light and various dipole-carrying excitations. The study directly proved the importance of the substrate's phonons in the photocurrent generation process. The performance of mid-IR graphene photodetectors is shown in Table 2.

Although graphene has an ultra-wide spectral bandwidth, the atomic layer thickness results in only ~2.3% absorption of the incident light which limits the responsivity of graphene photodetectors. One way to enhance the light absorption is to integrate graphene onto waveguide devices, in which the elongated optical interaction length can dramatically increase the absorption toward ~100% [40]. In our previous study, we proposed and demonstrated to use different structures, such as silicon slot waveguides [41] and silicon nitride microring resonators [42], to further enhance graphene to light interaction, as shown in Figs. 5 and 6. As waveguides are transparent in the mid-IR spectral region [43], ultracompact, waveguide integrated, mid-IR graphene photodetectors are a promising technology for the future.

4 Biochemical applications

With excellent optical and electronic properties, remarkable biocompatibility and ease of functionalization, graphene and its derivatives have received increasing attention in biochemical applications. In this section, we discuss recent experimental progress on mid-IR plasmonic sensing, photodynamic therapy, and fluorescence imaging applications.

Graphene plasmonics was first observed in the nanoribbon structure at the terahertz frequency in 2011 [44]. Since then, research efforts have been made to shift the

Table 2 Performance of mid-IR graphene photodetectors

reference	mechanism	responsivity	working bandwidth	wavelength
Mueller et al. [29]	photovoltaic effect	6.1 mA/W	10 GHz	up to 6 μm
Wang et al. [30]	photovoltaic effect	0.13 A/W		2.75 μm
Cheng et al. [31]	photovoltaic effect	4.5 mA/W		2.75 μm
Liu et al. [32]	photoconductive effect	1.1 A/W	1 KHz	3.2 μm
Zhang et al. [33]	photoconductive effect	0.4 A/W		10 μm
Yao et al. [34]	photoconductive effect	0.4 V/W	~6 MHz	4.45 μm
Hsu et al. [35]	photothermoelectric effect	7 – 9 V/W	~20 Hz	10.6 μm
Badioli et al. [36]	photothermoelectric effect			7.19 – 9.26 μm
Yan et al. [38]	bolometric effect	2×10^5 V/W	> 1 GHz	10.6 μm
Freitag et al. [39]	bolometric effect			6 – 12 μm

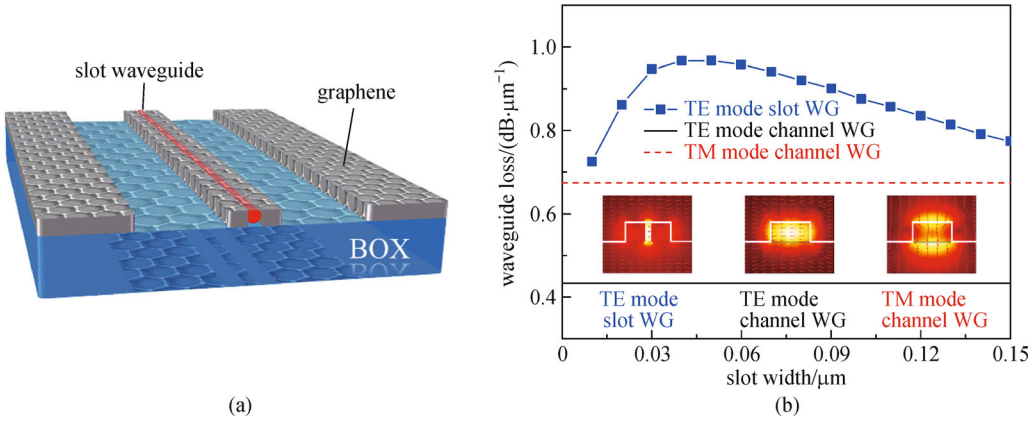


Fig. 5 Graphene on a silicon slot waveguide as a photodetector [41]. (a) Schematic picture of the photodetector; (b) absorption simulation of the photodetector. The inset shows energy distributions of different types of waveguides (WGs)

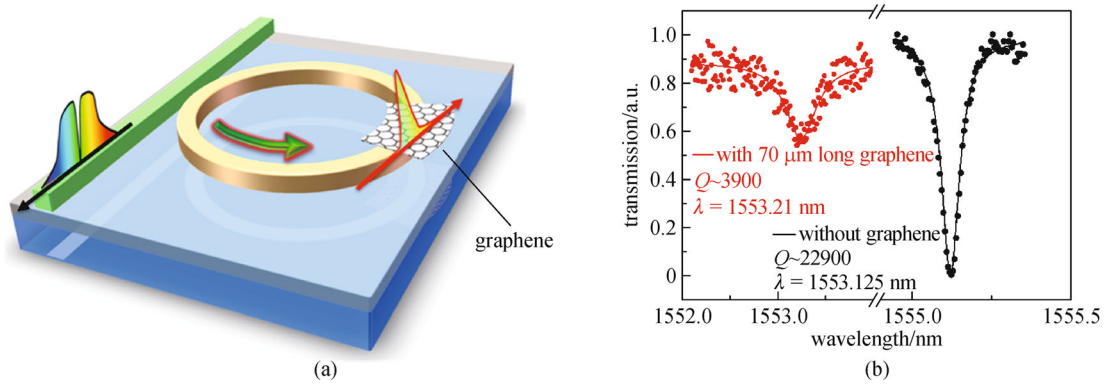


Fig. 6 Graphene on a silicon nitride microring resonator [42]. (a) Schematic picture of the resonator; (b) resonance spectra measurements and Lorentzian fittings

frequency of localized surface plasmon resonance (LSPR) to the mid-IR spectral region by using electrostatic or chemical doping and fabricating nanostructures, such as nanoribbons or nanodisks, on the graphene layer [45–47]. With the atomic layer thickness and the limited carrier density, graphene LSPR devices possess two excellent characteristics, namely ultrahigh light intensity confinement and frequency tunability, which make graphene serve as an excellent platform for ultrasensitive and tunable mid-IR sensors.

Based on the graphene nanoribbon structure, in 2014, Li et al. first used the near-field enhancement of light-matter interactions by graphene plasmons to probe the chemical bond information in the analyte [48]. They studied the interaction between graphene plasmons and vibrational modes in surface-adsorbed thin polymer films of poly (methylmethacrylate) and polyvinylpyrrolidone. The detection sensitivity was increased by a factor of ~5 compared to that of light attenuated by the carbonyl vibration alone. In 2015, Rodrigo et al. reported a high-sensitivity mid-IR plasmonic biosensor [49], which was used for chemically specific label-free detection of protein monolayers. Due to the dynamic tunable capability of the plasmonic resonant frequency, complex refractive index variations can be extracted from the plasmonic resonance shift and spectral dips with the amide I and II bands in the extinction spectra. This reveals the presence of the protein with chemical specificity. With great light intensity enhancement in the atomic layer thickness, the spectral shifts and absorption signals of graphene plasmonic sensors were demonstrated 6 times and 3 times larger than those obtained using metallic plasmonic sensors, respectively.

Since graphene can respond to photons in a broad spectrum [50], many graphene-based methods have been developed, such as lasers for imaging, drug delivery, and photodynamic therapy. Since the report from Dai Group that nano-graphene oxide (NGO) works for cellular imaging and drug delivery [51], a number of developments have been reported on this topic. Such NGO materials can easily be conjunct with other organic molecules to form complex and uptaken by cells. Therefore, they are natural carriers of molecules that can provide therapeutic effects such as oxidative stress to cells when they are activated by lasers. In this regard, NGO can be combined with other drugs as the carrier for drug delivery [52,53] and finally photodynamic therapy (PDT) [54,55]. Considering the direct absorption of NGO to lasers and the thermal effect, NGO itself can directly work as the PDT drug. The targeting process of NGO to diseased tissue or tumor can be achieved by immunomolecules or simply by metabolism [56,57]. After an uptake of NGO by the targeted cells or tissue, a higher thermal effect can be generated by IR laser irradiation which can then kill those cells or tissue [58–62]. The low toxicity of NGO is thus promising for clinic applications. NGO has a broad spectral bandwidth, various tissues with different optical properties and laser irradiation wavelengths are suitable for PDT [63,64].

Interestingly, during the research of PDT with graphene or NGO particles, it has been noticed that the graphene and NGO particles can emit visible-range fluorescence if the density of IR photons is high enough [65]. The multi-photon excitation was efficient and the fluorescence was stable due to the unique optical property of graphene. Therefore, graphene and NGOs are also widely used for in *vivo* multi-photon microscopy with ultrafast lasers [66], especially deep-tissue imaging [67]. Raman microscopy can also be achieved [68,69]. Importantly, these methods above can be achieved simultaneously by only graphene or NGOs [70].

5 Future prospective

The unique optical nonlinearities of graphene have shown great promises for enabling unprecedented ultrafast photonic capabilities in the mid-IR spectral region. In addition to enabling ultrafast bulk lasers, refined growth

and fabrication methods will open up new routes for realizing the new-generation of integrated lasers. Indeed, the success in using graphene to mode-lock a near-IR vertical-external-cavity surface-emitting laser (VECSEL) has demonstrated the potential for an all-integrated graphene mode-locked laser [71]. On the other hand, highly tunable Dirac fermions offer another important direction for further exploitation. Voltage-controlled devices have shown flexible parameter control capabilities in graphene-based optical devices [72]. Combining such a feature with other advanced photonic methods such as plasmonic nanostructures and micro-cavities can provide great flexibility in the design and optimization of photonic functional devices [73]. Extensive efforts are being made in this line of research and the impact is expected to be far reaching. Finally, it should be pointed out that graphene is not the only strategic material for the mid-IR range. Emerging materials such as 2D black phosphorus, which exhibits a small bandgap of ~ 0.3 eV, have also stimulated a great deal of research efforts in the area of mid-IR photonics. In addition to saturable absorbers, photodetectors and other photonic devices have been theoretically exploited and experimentally demonstrated [72–75].

6 Summary

In this article, we have reviewed recent experimental progress on mid-IR graphene photonics and biochemical applications. With the distinctive band structure and broadband spectral region, graphene has tremendous potential applications in the mid-IR photonics and biotechnology which have been hardly accessible using traditional materials. In the future, graphene photonics and its biochemical applications are anticipated to bring us exciting scientific and technological advances.

Acknowledgements This work was partly supported by MEXT Advanced Photon Science Alliance.

References

1. Schliesser A, Picqué N, Hänsch T W. Mid-infrared frequency combs. Nature Photonics, 2012, 6(7): 440–449
2. Jackson S D. Towards high-power mid-infrared emission from a fibre laser. Nature Photonics, 2012, 6(7): 423–431
3. Martinez A, Sun Z. Nanotube and graphene saturable absorbers for fire lasers. Nature Photonics, 2013, 7(11): 842–845
4. Keuleyan S, Lhuillier E, Brajuskovic V, Guyot-Sionnest P. Mid-infrared HgTe colloidal quantum dot photodetectors. Nature Photonics, 2011, 5(8): 489–493
5. Novoselv K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V, Firsov A A. Electric field effect in atomically thin carbon films. Science, 2004 , 306(5696): 666–669
6. Bonaccorso F, Sun Z, Hasan T, Ferrari A C. Graphene photonics and optoelectronics. Nature Photonics, 2010, 4(9): 611–622
7. Xia F, Yan H, Avouris P. The interaction of light and graphene: basics, devices, and applications. Proceedings of the IEEE, 2013, 101(7): 1717–1731
8. Ostojic G N, Zaric S, Kono J, Strano M S, Moore V C, Hauge R H, Smalley R E. Interband recombination dynamics in resonantly excited single-walled carbon nanotubes. Physical Review Letters, 2004, 92(11): 117402
9. Dawlaty J M, Shivaraman S, Chandrashekhar M, Rana F, Spencer M G. Measurement of ultrafast carrier dynamics in epitaxial graphene. Applied Physics Letters, 2008, 92(4): 042116
10. Hasan T, Sun Z, Wang F, Bonaccorso F, Tan P H, Rozhin A G, Ferrari A C. Nanotube polymer composites for ultrafast photonics. Advanced Materials, 2009, 21(38-39): 3874–3899
11. Bao Q, Zhang H, Wang Y, Ni Z, Yan Y, Shen Z X, Loh K P, Tang D Y. Atomic-layer graphene as a saturable absorber for ultrafast pulsed lasers. Advanced Functional Materials, 2009, 19(19): 3077–3083
12. Sun Z, Hasan T, Torrisi F, Popa D, Privitera G, Wang F, Bonaccorso F, Basko D M, Ferrari A C. Graphene mode-locked ultrafast laser. ACS Nano, 2010, 4(2): 803–810
13. Liu M, Yin X, Ulin-Avila E, Geng B, Zentgraf T, Ju L, Wang F, Zhang X. A graphene-based broadband optical modulator. Nature, 2011, 474(7349): 64–67
14. Yan H, Low T, Zhu W, Wu Y, Freitag M, Li X, Guinea F, Avouris P, Xia F. Damping pathways of mid-infrared plasmons in graphene nanostructures. Nature Photonics, 2013, 7(5): 394–399
15. Ju L, Geng B, Horng J, Girit C, Martin M, Hao Z, Bechtel H A, Liang X, Zettl A, Shen Y R, Wang F. Graphene plasmonics for tunable terahertz metamaterials. Nature Nanotechnology, 2011, 6 (10): 630–634
16. Wang Y, Li Z, Wang J, Li J, Lin Y. Graphene and graphene oxide: biofunctionalization and applications in biotechnology. Trends in Biotechnology, 2011, 29(5): 205–212
17. Feng L, Liu Z. Graphene in biomedicine: opportunities and challenges. Nanomedicine, 2011, 6(2): 317–324
18. Shen H, Zhang L, Liu M, Zhang Z. Biomedical applications of graphene. Theranostics, 2012, 2(3): 283–294
19. Yang K, Feng L, Shi X, Liu Z. Nano-graphene in biomedicine: theranostic applications. Chemical Society Reviews, 2013, 42(2): 530–547
20. Wang F, Torrisi F, Jiang Z, Popa D, Hasan T, Sun Z, Cho W, Ferrari A C. Graphene passively Q-switched two-micron fiber lasers. In: Proceedings of Conference of Lasers and Electro-Optics. 2012, 1–2
21. Zhang M, Kelleher E J, Torrisi F, Sun Z, Hasan T, Popa D, Wang F, Ferrari A C, Popov S V, Taylor J R. Tm-doped fiber laser mode-locked by graphene-polymer composite. Optics Express, 2012, 20 (22): 25077–25084
22. Ma J, Xie G Q, Lv P, Gao W L, Yuan P, Qian L J, Yu H H, Zhang H J, Wang J Y, Tang D Y. Graphene mode-locked femtosecond laser at 2 μm wavelength. Optics Letters, 2012, 37(11): 2085–2087
23. Lagatsky A A, Sun Z, Kulmala T S, Sundaram R S, Milana S, Torrisi F, Antipov O L, Lee Y, Ahn J H, Brown C T, Sibbett W, Ferrari A C. 2 μm solid-state laser mode-locked by single-layer graphene. Applied Physics Letters, 2013, 102(1): 013113
24. Cizmeciyan M N, Kim J W, Bae S, Hong B H, Rotermund F, Sennaroglu A. Graphene mode-locked femtosecond Cr:ZnSe laser

at 2500 nm. Optics Letters, 2013, 38(3): 341–343
25. Wang Q, Teng H, Zou Y, Zhang Z, Li D, Wang R, Gao C, Lin J, Guo L, Wei Z. Graphene on SiC as a *Q*-switcher for a 2 μm laser. Optics Letters, 2012, 37(3): 395–397
26. Tolstik N, Okhotnikov O, Sorokin E, Sorokina I T. Femtosecond Cr: ZnS laser at 2.35 μm mode-locked by carbon nanotubes. Proceedings of the Society for Photo-Instrumentation Engineers, 2014, 8959: 89591A
27. Wei C, Zhu X, Wang F, Xu Y, Balakrishnan K, Song F, Norwood R A, Peyghambarian N. Graphene *Q*-switched 2.78 μm Er^{3+}-doped fluoride fiber laser. Optics Letters, 2013, 38(17): 3233–3236
28. Zhu G, Zhu X, Wang F, Xu S, Li Y, Guo X, Balakrishnan K, Norwood R A, Peyghambarian N. Graphene mode-locked fiber laser at 2.8 μm. Photonics Technology Letters, 2016, 28 (1): 7–10
29. Mueller T, Xia F, Avouris P. Graphene photodetectors for high-speed optical communications. Nature Photonics, 2010, 4(5): 297–301
30. Wang X, Cheng Z, Xu K, Tsang H K, Xu J B. High-responsivity graphene/silicon-heterostructure waveguide photodetectors. Nature Photonics, 2013, 7(11): 888–891
31. Cheng Z, Wang J, Xu K, Tsang H K, Shu C. Graphene on silicon-on-sapphire waveguide photodetectors. In: Proceedings of Laser and Electro-Optics(CLEO), 2015
32. Liu C H, Chang Y C, Norris T B, Zhong Z. Graphene photodetectors with ultra-broadband and high responsivity at room temperature. Nature Nanotechnology, 2014, 9(4): 273–278
33. Zhang B Y, Liu T, Meng B, Li X, Liang G, Hu X, Wang Q J. Broadband high photoresponse from pure monolayer graphene photodetector. Nature Communications, 2013, 4: 1811
34. Yao Y, Shankar R, Rauter P, Song Y, Kong J, Loncar M, Capasso F. High-responsivity mid-infrared graphene detectors with antenna-enhanced photocarrier generation and collection. Nano Letters, 2014, 14(7): 3749–3754
35. Hsu A L, Herring P K, Gabor N M, Ha S, Shin Y C, Song Y, Chin M, Dubey M, Chandrakasan A P, Kong J, Jarillo-Herrero P, Palacios T. Graphene-based thermopile for thermal imaging applications. Nano Letters, 2015, 15(11): 7211–7216
36. Badioli M, Woessner A, Tielrooij K J, Nanot S, Navickaite G, Stauber T, García de Abajo F J, Koppens F H L. Phonon-mediated mid-infrared photoresponse of graphene. Nano Letters, 2014, 14 (11): 6374–6381
37. Wang J, Cheng Z, Chen Z, Xu J B, Tsang H K, Shu C. Graphene photodetector integrated on silicon nitride waveguide. Journal of Applied Physics, 2015, 117(14): 144504
38. Yan J, Kim M H, Elle J A, Sushkov A B, Jenkins G S, Milchberg H M, Fuhrer M S, Drew H D. Dual-gated bilayer graphene hot-electron bolometer. Nature Nanotechnology, 2012, 7(7): 472–478
39. Freitag M, Low T, Martin-Moreno L, Zhu W, Guinea F, Avouris P. Substrate-sensitive mid-infrared photoresponse in graphene. ACS Nano, 2014, 8(8): 8350–8356
40. Cheng Z, Tsang H K, Wang X, Xu K, Xu J B. In-plane optical absorption and free carrier absorption in graphene-on-silicon waveguides. IEEE Journal of Selected Topics in Quantum Electronics, 2014, 20(1): 4400106
41. Cheng Z, Wang J, Zhu B, Xu K, Zhou W, Tsang H K, Shu C. Graphene absorption enhancement using silicon slot waveguides. In: Proceedings of Photonics Conference (IPC) IEEE. 2015, 186–187
42. Wang J, Cheng Z, Shu C, Tsang H K. Optical absorption in graphene-on-silicon nitride microring resonator. IEEE Photonics Technology Letters, 2015, 27(16): 1765–1767
43. Cheng Z, Chen X, Wong C Y, Xu K, Fung C K, Chen Y M, Tsang H K. Focusing subwavelength grating coupler for mid-infrared suspended membrane waveguide. Optics Letters, 2012, 37(7): 1217–1219
44. Ju L, Geng B, Horng J, Girit C, Martin M, Hao Z, Bechtel H A, Liang X, Zettl A, Shen Y R, Wang F. Graphene plasmonics for tunable terahertz metamaterials. Nature Nanotechnology, 2011, 6 (10): 630–634
45. Fang Z, Wang Y, Schlather A E, Liu Z, Ajayan P M, de Abajo F J, Nordlander P, Zhu X, Halas N J. Active tunable absorption enhancement with graphene nanodisk arrays. Nano Letters, 2014, 14 (1): 299–304
46. Brar V W, Jang M S, Sherrott M, Lopez J J, Atwater H A. Highly confined tunable mid-infrared plasmonics in graphene nanoresonators. Nano Letters, 2013, 13(6): 2541–2547
47. Abbas A N, Liu G, Liu B, Zhang L, Liu H, Ohlberg D, Wu W, Zhou C. Patterning, characterization, and chemical sensing applications of graphene nanoribbon arrays down to 5 nm using helium ion beam lithography. ACS Nano, 2014, 8(2): 1538–1546
48. Li Y, Yan H, Farmer D B, Meng X, Zhu W, Osgood R M, Heinz T F, Avouris P. Graphene plasmon enhanced vibrational sensing of surface-adsorbed layers. Nano Letters, 2014, 14(3): 1573–1577
49. Rodrigo D, Limaj O, Janner D, Etezadi D, García de Abajo F J, Pruneri V, Altug H. Mid-infrared plasmonic biosensing with graphene. Science, 2015, 349(6244): 165–168
50. Loh K P, Bao Q, Eda G, Chhowalla M. Graphene oxide as a chemically tunable platform for optical applications. Nature Chemistry, 2010, 2(12): 1015–1024
51. Sun X, Liu Z, Welsher K, Robinson J T, Goodwin A, Zaric S, Dai H. Nano-graphene oxide for cellular imaging and drug delivery. Nano Research, 2008, 1(3): 203–212
52. Feng L, Yang X, Shi X, Tan X, Peng R, Wang J, Liu Z. Polyethylene glycol and polyethylenimine dual-functionalized nano-graphene oxide for photothermally enhanced gene delivery. Small, 2013, 9 (11): 1989–1997
53. Liu K, Zhang J J, Cheng F F, Zheng T T, Wang C, Zhu J J. Green and facile synthesis of highly biocompatible graphene nanosheets and its application for cellular imaging and drug delivery. Journal of Materials Chemistry, 2011, 21(32): 12034–12040
54. Tian B, Wang C, Zhang S, Feng L, Liu Z. Photothermally enhanced photodynamic therapy delivered by nano-graphene oxide. ACS Nano, 2011, 5(9): 7000–7009
55. Ma X, Tao H, Yang K, Feng L, Cheng L, Shi X, Li Y, Guo L, Liu Z. A functionalized graphene oxide-iron oxide nanocomposite for magnetically targeted drug delivery, photothermal therapy, and magnetic resonance imaging. Nano Research, 2012, 5(3): 199–212
56. Yang K, Zhang S, Zhang G, Sun X, Lee S T, Liu Z. Graphene in mice: ultrahigh in vivo tumor uptake and efficient photothermal therapy. Nano Letters, 2010, 10(9): 3318–3323
57. Huang P, Xu C, Lin J, Wang C, Wang X, Zhang C, Zhou X, Guo S, Cui D. Folic acid-conjugated graphene oxide loaded with photo-

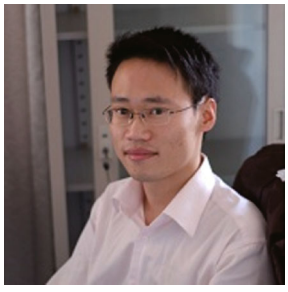
sensitizers for targeting photodynamic therapy. Theranostics, 2011, 1: 240–250
58. Li J L, Hou X L, Bao H C, Sun L, Tang B, Wang J F, Wang X G, Gu M. Graphene oxide nanoparticles for enhanced photothermal cancer cell therapy under the irradiation of a femtosecond laser beam. Journal of Biomedical Materials Research. Part A, 2014, 102(7): 2181–2188
59. Robinson J T, Tabakman S M, Liang Y, Wang H, Casalongue H S, Vinh D, Dai H. Ultrasmall reduced graphene oxide with high near-infrared absorbance for photothermal therapy. Journal of the American Chemical Society, 2011, 133(17): 6825–6831
60. Shi X, Gong H, Li Y, Wang C, Cheng L, Liu Z. Graphene-based magnetic plasmonic nanocomposite for dual bioimaging and photothermal therapy. Biomaterials, 2013, 34(20): 4786–4793
61. Akhavan O, Ghaderi E, Aghayee S, Fereydooni Y, Talebi A. The use of a glucose-reduced graphene oxide suspension for photothermal cancer therapy. Journal of Materials Chemistry, 2012, 22 (27): 13773–13781
62. Li M, Yang X, Ren J, Qu K, Qu X. Using graphene oxide high near-infrared absorbance for photothermal treatment of Alzheimer's disease. Advanced Materials, 2012, 24(13): 1722–1728
63. Yang K, Wan J, Zhang S, Tian B, Zhang Y, Liu Z. The influence of surface chemistry and size of nanoscale graphene oxide on photothermal therapy of cancer using ultra-low laser power. Biomaterials, 2012, 33(7): 2206–2214
64. Markovic Z M, Harhaji-Trajkovic L M, Todorovic-Markovic B M, Kepić D P, Arsikin K M, Jovanović S P, Pantovic A C, Dramićanin M D, Trajkovic V S. In vitro comparison of the photothermal anticancer activity of graphene nanoparticles and carbon nanotubes. Biomaterials, 2011, 32(4): 1121–1129
65. Li J L, Bao H C, Hou X L, Sun L, Wang X G, Gu M. Graphene oxide nanoparticles as a nonbleaching optical probe for two-photon luminescence imaging and cell therapy. Angewandte Chemie International Edition, 2012, 51(8): 1830–1834
66. Liu Q, Guo B, Rao Z, Zhang B, Gong J R. Strong two-photon-induced fluorescence from photostable, biocompatible nitrogen-doped graphene quantum dots for cellular and deep-tissue imaging. Nano Letters, 2013, 13(6): 2436–2441
67. Qian J, Wang D, Cai F H, Xi W, Peng L, Zhu Z F, He H, Hu M L, He S. Observation of multiphoton-induced fluorescence from graphene oxide nanoparticles and applications in in vivo functional bioimaging. Angewandte Chemie International Edition, 2012, 51(42): 10570–10575
68. Huang J, Zong C, Shen H, Liu M, Chen B, Ren B, Zhang Z. Mechanism of cellular uptake of graphene oxide studied by surface-enhanced Raman spectroscopy. Small, 2012, 8(16): 2577–2584
69. Liu Z, Guo Z, Zhong H, Qin X, Wan M, Yang B. Graphene oxide based surface-enhanced Raman scattering probes for cancer cell imaging. Physical Chemistry Chemical Physics, 2013, 15(8): 2961–2966
70. Yang K, Hu L, Ma X, Ye S, Cheng L, Shi X, Li C, Li Y, Liu Z. Multimodal imaging guided photothermal therapy using functionalized graphene nanosheets anchored with magnetic nanoparticles. Advanced Materials, 2012, 24(14): 1868–1872
71. Zaugg C A, Sun Z, Wittwer V J, Popa D, Milana S, Kulmala T S, Sundaram R S, Mangold M, Sieber O D, Golling M, Lee Y, Ahn J H, Ferrari A C, Keller U. Ultrafast and widely tuneable vertical-external-cavity surface-emitting laser, mode-locked by a graphene-integrated distributed Bragg reflector. Optics Express, 2013, 21(25): 31548–31559
72. Baylam I, Cizmeciyan M N, Ozharar S, Polat E O, Kocabas C, Sennaroglu A. Femtosecond pulse generation with voltage-controlled graphene saturable absorber. Optics Letters, 2014, 39(17): 5180–5183
73. Xia F, Wang H, Xiao D, Dubey M, Ramasubramaniam A. Two-dimensional material nanophotonics. Nature Photonics, 2014, 8(12): 899–907
74. Qin Z, Xie G, Zhang H, Zhao C, Yuan P, Wen S, Qian L. Black phosphorus as saturable absorber for the *Q*-switched Er:ZBLAN fiber laser at 2.8 μm. Optics Express, 2015, 23(19): 24713–24718
75. Youngblood N, Chen C, Koester S J, Li M. Waveguide-integrated black phosphorus photodetector with high responsivity and low dark current. Nature Photonics, 2015, 9(4): 247–252

Zhenzhou Cheng is currently an assistant professor of physical chemistry in the Department of Chemistry at the University of Tokyo. He received his B.S. degree in physics and M.S. degree in optics from Nankai University, China, in 2006 and 2009, respectively. He received his Ph.D. degree in electronic engineering from the Chinese University of Hong Kong in 2013. He was awarded the Young Scientist Award from Hong Kong Institute of Science in 2013. He joined the Department of Chemistry at the University of Tokyo as an assistant professor in 2015. His research focuses on graphene and silicon photonics for biomedical sensing and spectroscopy.

Changyuan Qin obtained her B.S. degree from Ludong University in 2011 and M.S. degree from Shanghai Normal University in 2014. She joined Professor Goda's group in the Department of Chemistry at the University of Tokyo as a research student in 2015. Her research focuses on chip-integrated Raman spectroscopy for biochemical sensing applications.

Fengqiu Wang obtained his Ph.D. degree in electrical engineering from the University of Cambridge in 2009. Prior to his Ph.D., he obtained his B.S. degree in electronics from Peking University, China. He is currently a professor of photonics in the School of Electronic Science and Engineering at Nanjing University, where his group is mainly focused on

developing novel optical and optoelectronic devices based on emerging nanomaterials for high-performance information photonic devices. Another key research area of the group is to study the photophysics of nanosystems using ultrafast spectroscopy in a broad spectral range, from EUV all the way to the mid-infrared. He has published over 50 research papers. His papers have drawn a total citation of over 3000 times. He is the principle investigator of two NSFC projects and co-investigator of one Key Basic Research Program of China, one National Key Scientific Instrument Development Project, as well as one ARC Discovery project (Australia). He serves as a technical committee member for top-tier international conferences on lasers and electro-optics, including CLEO 2016, CLEO-Pacific Rim 2015, OECC 2015. He is currently an associate editor for the journal *Scientific Reports*.



Hao He received his B.S. degree in optics from the University of Science and Technology of China in 2006 and Ph.D. degree in biophotonics from the Chinese University of Hong Kong in 2010. From 2011 to 2014, he worked at Tianjin University as an associate professor. Since 2014, he has been working as a professor at Shanghai Jiao Tong University, China. He mainly works on biophotonics utilizing femtosecond lasers for the modulation of cell molecular signaling and functions. He currently works on multiphoton microscopy, photostimulation to neurons and other cells, and apoptosis.

Keisuke Goda is currently a professor of physical chemistry in the Department of Chemistry at the University of Tokyo, an ImPACT program manager (Cabinet Office, Government of Japan), and an adjunct faculty member of electrical engineering at UCLA. He obtained his B.A. degree from UC Berkeley in 2001 and Ph.D. degree from MIT in 2007, both in physics. After several years of research at Caltech and UCLA, he joined the University of Tokyo as a professor in 2012. His research group (http://www.goda.chem.s.u-tokyo.ac.jp) focuses on the development of innovative methods for imaging and spectroscopy and the exploitation of novel applications for industry, green energy, and medicine. He was awarded Burroughs Wellcome Fund Career Award at the Scientific Interface, Konica Minolta Imaging Science Award, MEXT Young Scientist Award, and IEEE Photonics Society Distinguished Lecturers Award. In addition, he was selected by World Economic Forum as a Young Global Leader for recognizing his leadership in global education and research. He serves as an associate editor for *APL Photonics*.