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GRAPHENE COMPOSITES FOR ULTRAFAST PHOTONICS

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Abstract: *Ultrafast lasers play a key role in a variety of devices, from basic research to materials processing and medicine. Graphene has great potential as saturable absorber for ultrafast lasers. Here we present an overview of graphene-based ultrafast lasers, from solution processing of the raw materials, to their incorporation into polymers, device fabrication and testing.*

1. Introduction

Ultrafast lasers are essential tools in a myriad of applications, ranging from basic research and metrology to telecommunications, medicine, and materials processing [1]. Usually they are based on a mode-locking technique, whereby a nonlinear optical element – called saturable absorber (SA) – turns the laser continuous wave into a train of ultrashort pulses. Currently, semiconductor saturable absorber mirrors (SESAMs) are the most widely used SA [1,2]. However, SESAMs have a narrow tuning range (~ a few tens of nanometers [1,2]) and require complex fabrication and packaging [1]. Carbon nanotubes (CNTs) offer a simpler and cost effective alternative [3-12] as the operating wavelength is defined by their diameter (i.e. bandgap)[3] Tunability is possible by combining CNTs with a diameter distribution[5]. However, for a given wavelength, CNTs not in resonance are not used.

On the other hand, in graphene for any excitation there is always an electron–hole pair in resonance. Due to the ultrafast carrier dynamics [13,14] and large absorption of incident light ([15,16]), graphene behaves as a fast SA over a wide spectral range [3,17-19].

Here we discuss the potential of solution processed graphene and their polymer composites for convenient, economic and wideband ultrafast lasers.

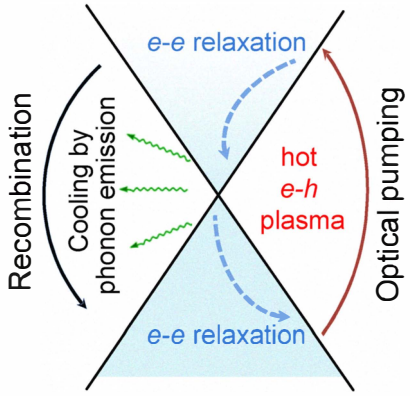

Fig. 1. Schematic illustration of photoexcited electron kinetics in graphene.

2. Optical properties

Graphene has promising optical properties [17]. Even though it is a single atom thick, graphene can be optically visualized [16,20]; its transmittance can be expressed in terms of the fine-structure constant [15]. It absorbs~2.3% of incident light per layer. Its absorption spectrum is quite flat from ultraviolet (UV) to infrared, with a peak at ~270nm, due to the exciton-shifted van Hove singularity in the graphene density of states [21]. This, in principle, allows graphene to be used for a very broad operation wavelength range (UV to THz).

Graphene also shows remarkable nonlinear optical properties [17]. Interband excitation by ultrafast optical pulses produces a non-equilibrium carrier population in the valence and conduction bands (Fig. 1). Time-resolved experiments [13] show two relaxation timescales: a faster one usually associated with carrier–carrier intraband collisions and phonon emission, and a slower one, on a ps timescale, which corresponds to interband relaxation and cooling of hot phonons [22,23].

3. Solution processing

Amongst the different approaches developed for graphene production [17] liquid phase exfoliation (LPE) of graphite [24-30] is an ideal means to achieve thin films and composites [3]. LPE graphene is exfoliated by ultrasonication (see Fig.2a), either in water [25-28] or in organic solvents [24,28,30].

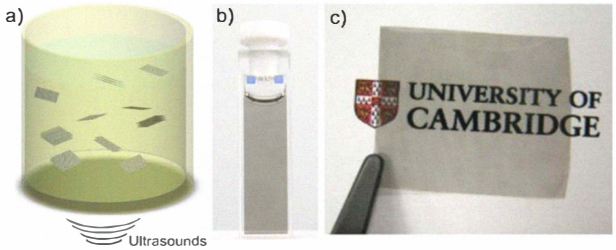

Fig. 2. a) Scheme of the exfoliation process. Photograph of b) graphene dispersion, c) graphene-polymer composite.

Pristine graphene flakes are hydrophobic and require surfactants for their dispersions in water [25-28]. Bile salts [31,32,34], amphiphilic molecules with a hydrophobic (β) and a hydrophilic ( ) side, are excellent dispersant agents, and prevents re-aggregation after the exfoliation process [27]. Sodium deoxycholate (SDC) forms a larger contact area per surfactant molecule [32] with respect to linear chain surfactants (e.g. sodium dodecylbenzene sulfonate (SDBS)[25]), which adsorb on graphitic surfaces through their alkyl chains [33]. Moreover, SDC has the highest hydrophobic index (HI) (i.e. the surface area ratio between β and side), amongst the bile salts [34]. High HI indicates stronger hydrophobicity [34], a key requirement in the adsorption of flat molecules onto the hydrophobic graphitic surface. The adsorption of SDC on graphite is also

thermodynamically favoured with respect to Sodium Cholate (SC)[28], determining a more stable dispersion. Indeed a higher percentage (~70%) of monolayer graphene can be obtained with SDC[17,27] rather than SC (19%)[29] or SDBS (3%)[25].

However, the presence of dispersant molecules is not the best option in view of their integration in devices when preservation of the pristine electronic structure is important. Also, the aqueous medium is not suitable for graphene integration into water-insoluble polymer composites. Therefore, much effort has been devoted to increase the concentration of graphene flakes dispersed both in high [24,28,30,35] and low boiling point [36] organic solvents. Graphitic flakes can be dispersed in organic solvents with up to $2gL^{-1}$ concentration [35].

4. Graphene polymer-composites

Graphene–polymer composites hold a great promise due to their advantages in fabrication and device integration compared to traditional semiconductor devices [3].

The choice of host polymer is fundamental in photonic applications. In addition to high optical transparency, laser damage threshold, thermal stability, the polymers must be easily processable during device fabrication and be economic [38]. Polymers traditionally used for optical applications include polymethylmethacrylate (PMMA) [37], polycarbonate (PC)[6] and epoxy resins [37]. Deuterated [38] or halogenated polyacrylates [38] and Fluorinated polyimides [37] have been developed to address specific iusses, such as optical losses [39], heat [38] and environmental stability[38]. Water-soluble polymers, such as polyvinylalcohol (PVA)[3,6] and cellulose derivatives, such as sodium carboxymethyl cellulose [3], have been widely used for CNT and graphene-based SAs [3-5,7,8] since stable, high-concentration dispersions can be readily prepared [3]. From the fabrication perspective, PVA is more attractive, because of its mechanical properties [3]. To prepare environmentally stable polymer composites, in particular, against humidity and temperature, graphene can be directly exfoliated in organic solvents [24]. The dispersions are suitable for moisture resistant polymers such as PC and PMMA or copolymers such as styrene methyl methacrylate [3].

Dispersion of graphene in solvents is the first step for the fabrication of polymer composites. The as-prepared dispersion (Fig.2b) is then mixed with the host polymer. The mixture is then drop-cast or spin coated to obtain free standing or substrate-bound graphene SA (GSA) composites with homogeneous, sub-micrometer distribution of graphene (see Fig.2c) [3,18,19,40,41]. A comprehensive review on the preparation and characterization of such polymer composites can be found in ref. [3].

5. Ultrafast lasers

Since their first demonstration [3], the performance of ultrafast lasers mode-locked by graphene has improved significantly: the average output power has increased by three-orders of magnitude from a few mW [3] to 1W[42]. Different production strategies (e.g. LPE [3,18,19,28,40,41], chemical vapour deposition (CVD)[17], carbon segregation [43], micromechanical cleavage [17,44,45]) have been used for GSA fabrication. Thus far, GSAs have been demonstrated for pulse generation at 1μm[17,52], 1.2μm [46], 1.5μm [18,19,28,44,45,49] and 2μm [47], the most common wavelength being ~1.5μm [18,19,28,44,45,49]. Ref. [19] reported a widely tunable fiber laser mode-locked with a GSA, Fig.3(a). The laser produces picosecond pulses in a 1525-1559nm tuning range.

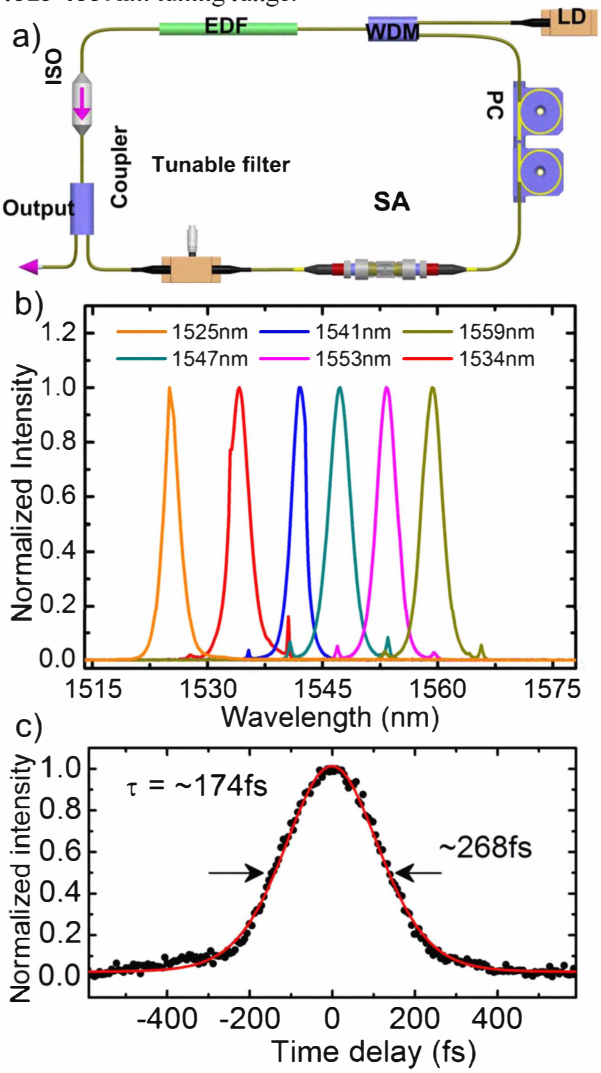

Fig.3. (a) Tunable GSA mode-locked ultrafast fiber laser setup Erbium doped fiber (EDF); Wavelength Division Multiplexer (WDM), Isolator (ISO), Polarization Controller (PC), (b) its output spectra and (c) Autocorrelation of typical output pulse.

Fiber lasers are attractive due to their efficient heat dissipation and alignment-free fiber format [48]. GSAs have been successfully used to mode-lock fiber lasers [3,17-19,44,45,49]. In this case, the simplest and most economical approach for GSA integration consists in sandwiching the GSA between two fiber connectors (Fig.3 (a)) [3,17-19,44,45,49]. Other approaches, such as evanescent-wave based integration [50], have also been

reported [17,50], especially for high-power pulse generation[17,50]. Sub-200fs (Fig.3 (c)) ultrafast pulses have been achieved using a stretched-pulse design [40].

Solid-state lasers are typically used for high-power output, as alternative to fiber lasers [51]. GSAs have also mode-locked solid-state lasers [17,52,53]. Large-area (>1cm^2) CVD graphene can be transferred on quartz substrates or high-reflectivity mirrors for solid-state laser mode-locking [17,46]. Ref. [46] reported 94fs pulse generation from a GSA mode-locked solid-state laser with 230mW output power. Another approach for GSA fabrication relies in spin-coating LPE graphene either on quartz substrates [17,42] or on high-reflectivity mirrors [17], which are then inserted into a solid-state cavity for ultrafast pulse generation. With this method, average power up to 1W was achieved using a solid-state Nd:YVO_4 laser [42]. The output wavelength was ~1μm with output energy ~14nJ [42].

6. Conclusions and outlook

Various laser systems (e.g. fiber and solid-state lasers) have been mode-locked using GSAs. In future, different types of ultrafast laser systems (e.g. waveguide, gas lasers, semiconductor,) could integrate GSAs. This will greatly expand the spectral coverage of GSA mode-locked ultrafast lasers (e.g. GSA mode-locked visible semiconductor lasers or mid-infrared CO_2/CO gas lasers). The optimization of GSA mode-locked laser design (e.g. high-order dispersion management) can generate output pulses as short as those produced by conventional SAs (e.g. SESAMs). High-repetition rate (>10GHz) ultrafast pulses are greatly needed for high-speed fiber communication [54]. Short (~mm) cavity can enable such high-repetition rate. The ease of fabrication and integration of GSA provides flexibility for short cavity designs. Graphene dispersions could be coated on the surface/facet of the gain sections (e.g. fiber, waveguide, semiconductor, monolithic solid-state gain materials). External-cavity pulse processing is another effective way to push the performances of GSA mode-locked ultrafast lasers [55]. For example, pulse compression, power amplification and frequency conversion can be employed for ultrafast (down to few-cycle), high-power (up to 100W or even higher) and broadband (e.g. from UV to THz) pulse generation [55].

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