



Black phosphorus polycarbonate polymer composite for pulsed fibre lasers

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ABSTRACT

Recently, the re-discovered black phosphorus (BP) has been extensively investigated for both electronic and photonic applications. However, the intrinsic instability of BP caused by moisture or oxygen reaction in ambient atmosphere has overshadowed its practical applications. Here, we present a liquid phase exfoliation-based approach for the production of few-layer BP (FL-BP) and the subsequent mixing with polycarbonate (PC) for the fabrication of a composite, which significantly reduces BP degradation by PC passivation. Experimentally, the functionalized PC few-layer BP (PC/FL-BP) composite shows environmental stability if compared with mechanically exfoliated BP flakes. We then use the PC/FL-BP composite as saturable absorber to study the nonlinear absorption property in a fibre laser at the 1.55 μm telecommunication wavelength. A Q-switched laser with pulse energy up to 25.2 nJ and pulse duration down to 1.65 μs is obtained at a low pump power of 71.7 mW. Our results can boost further research and scalable photonic applications, where environmentally stable few-layer BP based devices are needed.

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1. Introduction

Pulsed fibre lasers possess great advantages for various applications, if compared with pulsed solid-state lasers, such as telecommunication, sensing, spectroscopy, and medicine, due to their remarkable performance in terms of compactness, cost effectiveness, environmental insensitivity and effective thermal dissipation [1,2]. To date, the state-of-the-art pulsed laser technology is strongly dependent on the development of saturable absorbers (SAs), which are nonlinear optical components that enable pulse generation [3]. Currently, semiconductor saturable absorber mirrors (SESAMs) are dominating the SA market due to their excellent saturable absorption performance [3–5]. However, the complex fabrication and packaging technology of SESAMs makes them expensive devices [6,7]. Furthermore, SESAMs typically have only a few tens of nanometre operation bandwidth in the near-infrared region [5,8]. Thus, SAs based on new materials and

novel techniques offering complementary performance are highly desirable.

Recently, graphene [9–14] was experimentally identified as a promising SA for broadband ultrafast pulse generation in various laser systems (e.g., fibre [9–16], waveguide [17], solid-state [18,19], semiconductor [20] lasers) because of its unique properties and performance, such as fast recovery time [15], broad operation bandwidth [21–23], easy and cost-effective fabrication and integration [24]. Nevertheless, the weak optical absorption in graphene ($\sim 2.3\%$ for monolayer [25,26]) limits the modulation depth, which is a key parameter for ultrafast fibre lasers. Other two-dimensional (2D) crystals, such as transition metal di-chalcogenides (TMDs) (including MoS_2 [27–29], MoSe_2 [30], WS_2 [30]) have also been explored as SAs. Differently from graphene, these inorganic 2D crystals typically exhibit large band gap in their monolayer form (i.e., ~ 1.8 eV for MoS_2 , 1.7 eV for WSe_2 , 2.1 eV for WS_2), which are not suitable for fibre laser technology, generally operating in the near- and mid-infrared region [27,29,12]. Most recently, black phosphorus (BP), a layered crystal, has attracted great attention in electronics and photonics [12,31–34]. In contrast with graphene and many layered TMDs, BP presents a thickness dependent band gap tunability from 0.3 eV (in bulk) to ~ 1.5 eV (in monolayer) [12,35–37], which could bridge the gap between the zero band gap of graphene and the

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large band gap of layered TMDs [21]. Moreover, BP always shows direct band gap either in bulk or when exfoliated [32], enabling its application as an ideal semiconductor for electronics and photonics [31,38]. Inspired from graphene and other 2D crystals, the optical property of BP also attracts extensive interests [39–44]. Up to date, BP has been successfully utilized in pulsed laser generation ranging from near infrared ($\sim 1 \mu\text{m}$) to mid-infrared ($\sim 2.8 \mu\text{m}$) [39–44], demonstrating its broadband nonlinear optical responsivity.

Noteworthy, most of the demonstrated BP photonic devices (including those used for ultrafast lasers) [39–41,44] were based on BP produced by mechanical cleavage and used in ambient atmosphere. This determines a critical issue on the optical instability induced by the potential layer-by-layer etching derived from moisture [45] or oxidation reaction [46] within few layers BP (FL-BP). Moreover, the material erosion has been considered a critical point that could cause significant performance degradation in BP based optoelectronic devices [45–47], which are generally used in ambient conditions. To overcome this issue, various optimization strategies to protect and shield BP have been proposed [48–52]. For example, coating inert Al_2O_3 layers on BP by atomic layer deposition (ALD) method was studied to reduce the amount of the atmosphere/BP reactions by surface passivation [48,49]. Atomically-thick hexagonal boron nitride (*h*-BN) layer and polymethyl methacrylate (PMMA) film were also introduced to preserve the pristine performance of BP flakes [50–52] by encapsulation. However, ALD-based coating is not suitable for monolayer or FL-BP with low stability, because the ALD process may lead to rapid oxidation of the BP flakes [46,53]. Moreover, the fabrication of *h*-BN films and their use for BP encapsulation require rigorous parametric and environmental control [50,54], which significantly increases both cost and technological complexity. Overall, although these passivation methods are well implemented in devices, where BP is produced by micromechanical cleavage [39–41,44], they have drawbacks concerning large scale production and lack of flexibility due to the need of the transfer process to arbitrary substrates.

The weak interlayer interactions provide the possibility to produce FL-BP by solution processing approach [55]. In recent studies, it has been demonstrated that liquid phase exfoliation (LPE) is a scalable and cost-effective method for the production of FL-BP [56–59], opening the way to new applications based on functional polymer/FL-BP composites or functional inks [56,59]. In this work, we exploited LPE for the BP preparation and the subsequent realization of functional FL-BP composite blending with polycarbonate. Polycarbonate is selected because of its broad optical transparency in the visible and near-infrared range, a property previously exploited for the realization of composites for ultrafast lasers [60]. A long term optical absorption test in ambient atmosphere clearly shows that the PC/FL-BP composite is more stable than the mechanically exfoliated BP flakes. We then integrate the PC/FL-BP composite into a fibre laser at $1.55 \mu\text{m}$, the telecommunication wavelength, for Q-switching operation. Large energy pulses with pulse energy up to 25.2 nJ and pulse duration down to $1.65 \mu\text{s}$ are generated at the maximum pump power of 71.7 mW . These results demonstrate the effective nonlinear optical property of our functional PC/FL-BP composite, paving the way for the practical implementation of FL-BP in photonic and optoelectronic applications.

2. Black phosphorus polymer composite fabrication

2.1. Selection of solvents for the black phosphorus exfoliation

By using the approximation $\gamma = E - T \times S$ (where γ is the surface tension, E is the surface energy, T is the absolute temperature, and S is the solvent surface entropy, which generally takes a value of

$0.1 \text{ mJm}^{-2} \text{ K}^{-1}$ [61,62]), we can select the “right” solvent by estimating γ needed to exfoliate bulk BP and get a stable dispersion of FL-BP. The E of BP is $\sim 60 \text{ mJm}^{-2}$ [63]. Therefore, a solvent with a γ of $\sim 30 \text{ mJm}^{-2}$ is needed for the exfoliation of bulk BP, which is deduced by replacing the E of BP in the aforementioned equation at room temperature (i.e., 300 K). *N*-Cyclohexyl-2-pyrrolidone (CHP), having a γ of 37 mJm^{-2} [64] is then considered an appropriate solvent for the LPE process of BP, starting from the exfoliation of bulk BP and the preparation of FL-BP dispersion [56].

2.2. Black phosphorus exfoliation process

100 mg of bulk BP crystals (centimetre size, from Smart Elements) are crushed, using a mortar inside a glovebox, to reduce size and get a powder-like sample. Before performing the LPE process, the powder-like BP is dispersed in 100 mL of CHP (Sigma Aldrich, boiling point: 284°C) and dispersed by using an ultrasonic bath for 6 h. The ultra-sonicated BP in CHP solution is then centrifuged at $\sim 560g$ in a Sigma 3–16KL centrifuge for 180 min, exploiting the sedimentation-based separation (SBS) process [11,56,61,65–67,68], to separate thick and/or un-exfoliated BP flakes from the thinner ones.

2.3. Few-layer BP polycarbonate composite

For the realization of the BP-based composite, the LPE BP flakes in dispersion are then mix with polycarbonate. To obtain a completely dry composite, the blending with BP flakes and polycarbonate requires the removal of the solvent [11,60,69–71]. However, the CHP removal by direct evaporation is unfeasible in our process because the high boiling point of CHP (284°C) determines polycarbonate degradation (melting point 155°C , glass transition temperature: 147°C [72]). Contrary, chloroform has a low boiling point (61°C) and is also a solvent able to disperse polycarbonate [73]. Unfortunately, it is not possible to exfoliate bulk BP directly in chloroform, due to the lack of the required physical-chemical properties, such as γ , as discussed in aforementioned paragraph [67]. Thus, we carried out a solvent exchange process by using centrifugation [68,74] to remove the CHP and re-disperse the exfoliated BP flakes in chloroform. In the solvent exchange process, 20 mL of chloroform (from Sigma Aldrich) are added to the BP-based CHP dispersion and centrifuged at $560g$, successively 90% of the supernatant is discarded and the precipitate is re-suspended in 20 mL of chloroform. This CHP removal procedure is repeated 4 times to optimize the process. Finally, the precipitate is re-suspended in 5 mL of chloroform and dispersed by using an ultrasonic bath for 5 min. The entire solvent exchange process is carried out under inert atmosphere. For the realization of the composite, 100 mg of polycarbonate pellets (Molecular weight: 45 000, from Fisher) are dispersed in 10 mL of chloroform via stirring process. Subsequently, 1 mL of the BP-based chloroform dispersion and 2 mL of polycarbonate in chloroform are mixed. After the solvent evaporation at room temperature, the experimentally available PC-BP composite is obtained. This procedure has several advantages with respect to the exfoliation of 2D crystals in the target solvent [66–68]. First, it allows the exfoliation of the layered materials (i.e., BP) in the solvent with the required physical-chemical properties (e.g., γ and viscosity), obtaining a dispersion with high quality (e.g., both by weight and single layer percentage) [24]. Second, it allows changing the solvent on-demand, according to the target application, i.e., change to a non-toxic solvent for electronic applications [68] or organic solvents for polymer dispersion [75]. Third, it is also possible to tune on demand the concentration of the obtained dispersion [76], according to the final application.

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