Graphitic nanosheets via two-dimensional polymerization enhancing organic all-optically controlled photorefractive performance

Yingliang Liu^{1,2} · Weiwei Zuo¹ · Mingming Li¹ · Juan Li¹ · Shengang Xu^{1,2} · Shaokui Cao^{1,2}

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Abstract

All-optically controlled devices are the attractive subjects due to their future applications in all-optically controlled networks and computers. In this work, two-dimensional (2D) graphite nanosheets are synthesized to improve organic photorefractive performance in the all-optical operation, i.e., the photorefractive performance under zero electric field. The synthetic process is performed by 2D-polymerizing electrophilic and nucleophilic carbon species under solvothermal effect, where $[\text{:C}\equiv\text{C:}]^{2-}$ in calcium carbide is applied as nucleophilic carbon species and $[\text{C}(\text{Cl})]$ in carbon tetrachloride (CCl_4) as electrophilic carbon species. The polycarbonization reaction consists of 1D horizontal growth for nanoribbon and 2D vertical growth for single-layer graphene. Then, single-layer graphene nanosheets are aggregated via π - π stacking effect into 2D graphite nanosheets being composed of multilayer graphene nanosheets. Notably, the self-template characteristics induce the synchronous and alternate ongoing of three above processes. Interestingly, when these 2D graphite nanosheets are doped into organic photorefractive devices, the all-optically controlled photorefractive performance is effectively improved by enhancing the gain coefficient of two-beam coupling about 46.4% from 80.1 cm^{-1} of control device to 117.2 cm^{-1} of nanographite-doped device. This is attributed to the excellent electric conductance of 2D graphite nanosheets, which strengthens the charge separation under the nonuniform light field inside organic photorefractive devices. Then, the stronger built-in electric field will be induced so that the orientation enhancement effect is increased in organic photorefractive devices. This work provides an effective and facile approach to improve organic all-optically controlled photorefractive performance with 2D graphitic nanosheets.

Weiwei Zuo and Mingming Li have contributed equally to this work.

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✉ Yingliang Liu, liuylxn@zzu.edu.cn; ✉ Shengang Xu, xusg@zzu.edu.cn; ✉ Shaokui Cao, caoshaokui@zzu.edu.cn | ¹School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, People's Republic of China. ²Henan Key Laboratory of Advanced Nylon Materials and Application, Zhengzhou University, Zhengzhou 450001, People's Republic of China.

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Graphic abstract

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1 Introduction

All-optically controlled devices, which control the light using light without other external fields like electric field, are presently the attractive subjects [1–7] due to their potential applications in the future all-optically controlled networks and computers for all-optical signal processing, such as storage, amplification, interchange, combination and separation. They are deemed to have the potential to break through the limitation of electronic bottleneck in the traditional electronic devices [1], realizing the next generation of high-speed information transportation and high-capability information processing in the broader operating bandwidth. Among them, All-optically controlled photorefractive (AOC-PR) device without external electric field is an important photonic device for all-optical signal processing in the integrated photonic chips [8–15].

The PR effect is based on the first-order electro-optic effect, also known as Pockels effect or Kerr effect, which is the nonlinear change in refractive index in the noncentrosymmetric materials induced by the direct current (DC) field [16–20]. The PR processes consist of nonuniform light formation, exciton generation, charge-separated diffusion, built-in electric-field formation, refractive index modulation and optical signal processing. All these processes are generally performed under an external electric field. Through our continuous attempts over the years [8–10], the external electric field is regarded to be unnecessary for the PR effect, which is defined as all-optically controlled photorefractive effect. On the basis of above PR processes, it was found that the diffusion of separated charges is a key issue to strengthen the built-in electric field in the PR

devices [8], which is an important factor to enhance the orientation enhancement effect in organic photorefractive devices.

It was well known that the charge diffusion depends on the electric conductance in organic photorefractive device [17, 20], which might be strengthened by excellent electric conductors. In this case, the 2D carbonaceous materials are able to be applied as the electric conductor to strengthen the built-in electric field in organic photorefractive devices [21–24], similarly to inorganic nanowires [25–31]. At the same time, the size of 2D carbonaceous materials is an important factor to guarantee the strengthening of built-in electric field, instead of quenching. As for the microscopic structure of photorefractive gratings, the size of 2D carbonaceous materials should be less than the photorefractive grating period Λ , which could be calculated by $\Lambda = \lambda/2 \sin(\theta/2)$ [20] where θ is the interception angle of two interfering beams. Without question, the bottom-up chemical synthesis starting from organic building blocks should be an effective approach to control the size of 2D carbonaceous materials [32]. To date, several bottom-up strategies about the chemical synthesis of 2D carbonaceous materials have been reported, such as solution synthesis [33], surface-mediated synthesis [34–37] and chemical vapor deposition (CVD) synthesis [38]. However, the most striking synthetic approach is still the wet chemical mean [39] independent of ultra-high vacuum (UHV) despite the existing of strong aggregation derived from intermolecular π – π stacking [40].

In this work, to improve organic AOC-PR performance, the graphitic nanosheets are prepared as 2D carbonaceous materials through the 2D-polymerization reaction

of nucleophilic substitution reaction of carbon-halogen bond with nucleophilic carbon species due to the formation of C–C bond. The excellent electric conductance of 2D graphitic nanosheets will strengthen the charge separation under the nonuniform light field inside organic photorefractive devices. As a result, the stronger built-in electric field will come into being so that the orientation enhancement effect in organic AOC-PR devices should be increased to afford the larger gain coefficient of two-beam coupling under zero electric field.

2 Experimental section

2.1 Instruments and characterization

The TEM images are achieved on JEM-2100 high-resolution transmission electron microscopy by JEOL Ltd., whose sample is fabricated by dropping the ethanol solution of 2D graphitic nanosheets on the formvar stabilized with carbon support films. The SEM images are observed from JSM-7500F field emission scanning electron microscopy by JEOL Ltd., whose sample is fabricated by dropping the ethanol solution of 2D graphitic nanosheets on the silicon wafer. The X-ray diffraction is measured at a scanning speed of 10°/min on a *D/max 2500* XRD diffractometer (Rigaku) with Cu K α radiation (0.1541 nm). The IR spectra are recorded on TENSOR II Fourier transform infrared spectrometer with an integrated platinum-ATR-accessory. The UV–Vis–NIR spectra are monitored on an ultraviolet–visible–near-infrared Cary5000 spectrophotometer by Agilent Technologies. The Mott–Schottky curves are tested on a RST5000 electrochemical workstation. The Raman spectra are recorded on a DXRxi Raman imaging microscope by ThermoFisher Scientific Corporation.

2.2 Reagents

Calcium carbide (CaC₂) is purchased from Sigma-Aldrich Chemical Corporation. Carbon tetrachloride (CCl₄) is bought from Chinese chemical companies and purified to eliminate the impurity of carbon disulfide. The specific procedure is given below: Carbon tetrachloride (500 mL), potassium hydroxide (30 g) and ethanol (95%) are mixed in a 1000-mL round flask. After shaking for 30 min in the table concentrator, the solution is distilled and washed with distilled water. Then, the above procedure is performed again except that the amount of potassium hydroxide is reduced in half. The residual ethanol and water in the purified carbon tetrachloride are removed using anhydrous calcium chloride. After filtration, carbon tetrachloride is evaporated under reduced pressure and gathered through

condensation. Finally, the purified carbon tetrachloride is kept under molecular sieve for use.

2.3 Synthetic procedure of 2D graphitic nanosheets

Calcium carbide and carbon tetrachloride are added at an equivalent mass ratio into a 50-mL autoclave, where $[\text{C}\equiv\text{C}]^{2-}$ is regarded to be two functionality nucleophilic monomer and CCl₄ to be four functionality electrophilic monomer according to the principle of polymer chemistry. Then, the autoclave is sealed and heated to 250 °C in a salt bath. After the polycarbonization reaction is carried out for 10 h, the as-synthesized product is washed with a large number of hydrochloric acid (3 wt%). After filtrating and freeze-drying, the black solid powder is obtained.

2.4 Fabrication of photorefractive devices

Organic photorefractive composite film was fabricated by solution casting approach. Firstly, organic photorefractive compound **CRA-CSN₇₅-Cz₂₅** and ethylcarbazole (**ECZ**) were respectively dissolved in THF at a concentration of 5 mg/mL. The photosensitizer (**PC₆₁BM**) was also prepared as a THF solution. Afterward, the solutions of **CRA-CSN₇₅-Cz₂₅**, **ECZ** and **PC₆₁BM** were mixed according to a certain volume proportion and filtrated by a PTEF filter with a pore of 0.2 μm . After a majority of solvent was evaporated, the solution was dropwise added on the ITO substrate, which was heated to 40 °C with a digital hot plate in order to speed up the solvent evaporation. The residual solvent was naturally evaporated under good ventilation. Subsequently, the solid sample was dried overnight in vacuum in order to remove the residual solvent. After that, another piece of ITO glass was covered on the solid sample at 70 °C, where the potential crystal will be eliminated. The photorefractive composite film was immediately pressed, while the film thickness was controlled through a spacer of 80 μm . Finally, the photorefractive device was suddenly cooled down to keep the photorefractive composite film in a good amorphous state. The fabricated devices were kept in the refrigerator for the photorefractive characterization.

Nanographite-doped photorefractive devices were also fabricated according to the above procedure except that 2D graphitic nanosheets were doped into organic photorefractive composites with a 0.3 wt% ratio before the solution was filtrated by a PTEF filter.

2.5 Photorefractive characterization

The photorefractive performance was investigated by the two-beam coupling (TBC) experiments under zero external electric field. A tilted grating is written inside the photorefractive devices at oblique incidence angles. Two

p-polarized beams (Beam 1: 8 mW; Beam 2: 16 mW) with a wavelength of $\lambda = 633$ nm, which are obtained by a non-polarized beam splitter, are crossed inside the device at external incidence angles of 30° and 60° . The total power of modulated transmitted signals is monitored by identical photodetectors and recorded by a digital oscilloscope. The coupling gain coefficient (Γ) in the all-optical operation is calculated with the following formula [9]:

$$\Gamma = d^{-1} \cos \theta_{in} [\ln(\gamma_0 \beta) - \ln(\beta + 1 - \gamma_0)]$$

where d is the sample thickness, θ_{in} is the incident angle of Beam 1 inside the sample, β is the initial intensity ratio of beams after the sample in the absence of coupling, and γ_0 is the beam-coupling ratio (I/I_0). Here, I_0 is the signal intensity without the pump beam. I is the signal intensity with the pump beam.

3 Results and discussion

3.1 Synthesis of 2D graphitic nanosheets

Due to the excellent electric conductance of 2D carbonaceous materials, the 2D graphitic nanosheets are synthesized in this work through the 2D-polymerization reaction of nucleophilic substitution reaction of carbon–halogen bond with nucleophilic carbon species. The aim is to improve organic AOC-PR performance by strengthening the built-in electric field for stronger orientation enhancement effect of organic photorefractive materials. Herein, $[\text{C}\equiv\text{C}]^{2-}$ in calcium carbide is used as nucleophilic carbon species, while $[\text{C}(\text{Cl})_4]$ in carbon tetrachloride (CCl_4) is applied as electrophilic carbon species, as shown in the chemical formula of Scheme 1. As a consequence, the 2D graphitic nanosheets are achieved as shown in the digital photograph of Scheme 1 through the polymerization reaction of $[\text{C}\equiv\text{C}]^{2-}$ with CCl_4 consisting of 1D horizontal growth for carbonaceous nanoribbon, 2D vertical growth for graphene nanosheet and π – π stacking interaction for 2D graphitic nanosheet. The full-scale XPS spectrum in Fig. 1a indicated that 2D graphitic nanosheets are made of carbon (C1s: 284 eV), oxygen (O1s: 532 eV) and chlorine (Cl2p: 201 eV; Cl2s: 272 eV) elements. We inferred that the existence of oxygen element in the 2D graphitic nanosheets is derived from the hydrolysis of C–Cl bonds producing the oxygen-containing groups of OH, CHO and COOH, which are further proved by their characteristic signals in the IR spectrum of Fig. 2a.

According to the conception of polymerizable functional groups of the monomers in polymer chemistry, the polymerization system of $[\text{C}\equiv\text{C}]^{2-}$ and $[\text{C}(\text{Cl})_4]$ belongs to the (A2 + B4) synthetic strategy of hyperbranched or

Scheme 1 Diagrammatic sketch of synthetic strategy for 2D graphitic nanosheets (inset: digital photograph of as-prepared sample). Note: Nu nucleophilic carbon species; El electrophilic carbon species; Ca the carbene species as an auxiliary species

Fig. 1 Full-scale XPS spectrum (a B.E.: binding energy), XRD pattern (b) and Raman spectrum of 2D graphitic nanosheets

Fig. 2 IR spectrum (a), UV-Vis-NIR absorption spectrum (b) and Mott-Schottky curves (c) of 2D graphitic nanosheets

cross-linked polymer [41, 42] if $[:C\equiv C:]^{2-}$ is regarded as a two-functional monomer (one functionality per lone pair electrons) and CCl_4 is considered to be a four-functional monomer (one functionality per C-Cl bond). If this polymerization system follows the conventional principles of polymer chemistry for hyperbranched or cross-linked polymer, the three-dimensional (3D) chemical structure will be achieved as depicted in Scheme S1. However, our

experimental results are not entirely the case as mentioned above. Through our careful characterization and analysis, we confirmed that the polymerization of $[:C\equiv C:]^{2-}$ and CCl_4 in this work follows the 2D planarly oriented polymerization for 2D carbonaceous materials with excellent electric conductance as described in Scheme S2. The 2D laminated structure is confirmed by the strong (002, $2\theta = 26.5^\circ$) and weak (004, $2\theta = 54.6^\circ$) diffraction signals [43, 44] in the XRD patterns of Fig. 1b, which are the characteristic signal of typical laminated carbonaceous materials. The sharp and shoulder signal at 2692 cm^{-1} in the Raman spectra of Fig. 1c indicated the 2D graphitic nanosheets mainly consist of multilayer graphene [45]. In addition, the 2D graphitic nanosheets show the wide absorption property up to the near-infrared region as illustrated in Fig. 2b, which is derived from their 2D conjugated electronic structure. The negative flat band voltage of -0.81 V in the Mott-Schottky curves of Fig. 2c indicates the electron-rich feature of 2D graphitic nanosheets. These results suggest the excellent absorption and electron-donating properties, which is propitious to the generation and diffusion of photo-generated carriers to strengthen the built-in electric field for the improvement in organic AOC-PR performance.

The 2D planarly oriented polymerization of electrophilic and nucleophilic carbon species is regarded as a kind of bottom-up wet chemical strategy of polycarbonization reaction. The specific polymerization mechanism is divided into several substeps as shown in the diagrammatic sketch of Scheme 1. Their specific chemical processes are described in detail as illustrated in Scheme S2: the first is involved in the generation of carbonaceous nanoribbon, i.e., the horizontally growing process ladder carbonaceous polymer, through a series of elementary reactions including the substitution reaction and carbene-assisted cyclizing reaction [46, 47], where carbene species ($R_1R_2C:$) are in situ generated in the solvent of carbon tetrachloride under solvothermal effect; the second is related to the extension of carbonaceous nanoribbon, i.e., the vertically growing process of graphene nanosheet, through continuous coupling reaction being assisted by carbene on the edge of carbonaceous nanoribbon; the final step is the stacking of graphene nanosheets through the π - π interaction between different graphene nanosheets, presenting 2D graphitic nanosheets. A few of graphene nanosheets pointed out by the arrow in Fig. 3a imply that the 2D graphitic nanosheets are derived from the π - π stacking interaction of different graphene nanosheets. Notably, it is impossible that the substeps mentioned above are individually performed in turn. In fact, the horizontally growing for carbonaceous nanoribbon and the vertically growing for graphene nanosheet are alternately ongoing, which is identified by the irregular and hierarchical edge of multilayer graphene in the SEM images of 2D graphitic

Fig. 3 SEM images of 2D graphitic nanosheets

nanosheets in Fig. 3b. At the same time, we also found in Fig. 3b that the most of 2D graphitic nanosheets bear the size from several tens of nanometer to several hundreds of nanometer, which is less than photorefractive grating period Λ of 1.2 μm in this work produced by the 633 nm laser in our optical route for photorefractive measurement.

In the process of polycarbonization reaction, the kinetically motive power, which drives the polymerization of $[:\text{C}\equiv\text{C}:]^{2-}$ and CCl_4 toward the 2D planarly oriented polymerization instead of 3D polymerization, is its self-template feature caused by the static interaction of electron-deficient C–Cl bonds on the edge of growing graphene nanosheet with electron-rich graphene nanosheet. The self-template feature of 2D planarly oriented polymerization in the process of polycarbonization reaction is

evidently affirmed by the growing carbonaceous nanoribbon on the graphene nanosheet as shown in the TEM image of Fig. 4a, b, together with the hierarchical edge labeled by an arrow in the TEM images of Fig. 4c. This self-template feature was applied in a single-crystal ferroelectric nanoplate [48]. We can imagine that the template inducing the 2D planarly oriented growing of carbon species in the process of previous graphene synthesis is provided by a certain metal surface, such as Ag (111), Au (111) and Cu (111) [40]. In this work, the template guiding the carbon species to 2D planarly polymerization is presented by the surface of electron-rich graphene nanosheets.

The above polymerization processes are also monitored by the HRTEM image. Figure 4d shows a lot of stripe-like carbonaceous structure, which are regarded to be some carbon species for nucleophilic $[:\text{C}\equiv\text{C}:]^{2-}$ and electrophilic C(Cl) to be incompletely put into the crystal lattice of graphene. These quasi-order carbon species are able to be observed more clearly in the magnified HRTEM image of Fig. 4e and very similar to the ordered carbon atoms in the graphene nanosheet as shown in the 3D model of Fig. 4f. When the carbon species is completely put into the crystal lattice of graphene further forming 2D graphitic nanosheets in Fig. 4c, the diffraction pattern of honeycomb-like hexagonal structure is illustrated in the inset of Fig. 4d. These results fully proved that 2D graphitic

Fig. 4 TEM and HRTEM images of 2D graphitic nanosheets (a) surfacial image; (b) magnified image in the square frame of a; (c) edge image; (d) magnified image in the square frame of d; the inset in d: is the diffraction pattern; (e) magnified image in the square frame of d; the inset in d: is the diffraction pattern; (f) 3D model of graphene)

nanosheets are synthesized by 2D-polymerizing the electrophilic and nucleophilic carbon species as described in the diagrammatic sketch of Scheme 1 and the specific chemical route of Scheme S2.

3.2 Nanographite-doping photorefractive devices

According to our initial experimental design to improve organic AOC-PR performance, the 2D electron-rich graphitic nanosheets synthesized in this work are doped into organic photorefractive composite **CRA-CSN₇₅-Cz₂₅/ECZ/PC₆₁BM** (69:30:1) before the solution of photorefractive composites was filtrated by a PTEF filter. The aim is to guarantee the effective interaction between photorefractive compound **CRA-CSN₇₅-Cz₂₅** and photosensitizer **PC₆₁BM** avoiding the electrostatic association of electron-deficient **PC₆₁BM** and electron-rich 2D graphitic nanosheets. This is also propitious to the effective exhibition of bridge-conducting action of 2D graphitic nanosheets in organic photorefractive composites [49–52]. The digital photograph of photorefractive devices is shown in Fig. 5a. To confirm the ability of optical transmittance, the laser goes through the photorefractive devices as illustrated in Fig. 5b. The result indicated the all the photorefractive devices have an excellent optical transmittance due to the glassy morphology of organic photorefractive compound **CRA-CSN₇₅-Cz₂₅** [53], which is a necessary condition to form the photorefractive grating inside organic photorefractive composites.

The coupling gain coefficient (Γ) in the AOC-PR photorefractive devices is measured to be 80.1 cm^{-1} by the two-beam coupling (TBC) experiments under zero external electric field through the externally and internally plasticizing optimization of AOC-PR performance [53]. The chemical structures of **CRA-CSN₇₅-Cz₂₅**, **ECZ** and **PC₆₁BM** are shown in Fig. 6. Among them, the branched hyperstructure of **CRA-CSN₇₅-Cz₂₅** is to ensure the morphology of organic photorefractive molecular glass with high optical transparency [54–56], which will produce a strong nonuniform light field inside organic photorefractive

Fig. 5 Digital photograph (a) and laser-transmitting illustration (b) of prepared photorefractive devices

Fig. 6 The chemical structures of **CRA-CSN_x-Cz_(100-x)** (here, $x = 75$), **ECZ** and **PC₆₁BM**

composites to more effectively form the periodic built-in electric field. **ECZ** is applied as a plasticizer, and **PC₆₁BM** as a photosensitizer. The optical route of TBC experiments is illustrated in Fig. 7a where two interfering lights go through organic photorefractive composites to form the periodic photorefractive gratings as shown in Fig. 7b. Then, the built-in electric field is produced through the diffusion of photo-generated carriers under nonuniform light field as displayed in Fig. 7c in order to afford a necessary condition for the orientation enhancement effect of organic photorefractive chromophores.

In this work, the unique purpose to dope the 2D graphitic nanosheets into **CRA-CSN₇₅-Cz₂₅/ECZ/PC₆₁BM** is to further improve its AOC-PR performance by strengthening the built-in electric field as shown in Fig. 7c, which might be produced by the more effective diffusion of photo-generated carriers owing to the excellent electric conductance of 2D graphitic nanosheets. As a result, the orientation action of organic photorefractive chromophores is increased, i.e., the orientation enhancement effect is strengthened. Notably, to avoid the quenching effect in this work, the size of 2D graphitic nanosheets is controlled to be less than the photorefractive grating period Λ of $1.2 \mu\text{m}$, which is produced by the 633 nm laser in our photorefractive measurement.

First of all, the UV–Vis spectra of **ECZ/PC₆₁BM** and **CRA-CSN₇₅-Cz₂₅/ECZ/PC₆₁BM** in the solid film, which are prepared by spin-coating the dilute solution on the ITO substrate, are measured as illustrated in Fig. 8. The 2D graphitic nanosheets are doped into organic photorefractive composites in order to investigate the interaction between the photorefractive composite and 2D graphitic nanosheets. Figure 8a shows the same sharp $n-\pi$ and $\pi-\pi$ absorptions of carbazole groups at 347 nm and 332 nm in the UV–Vis spectra of **ECZ/PC₆₁BM** and nanographite-doped **ECZ/PC₆₁BM**. The doping of 2D graphitic nanosheets into **ECZ/PC₆₁BM** only enhances the absorption at the long wavelength but does not change the absorption feature of

Fig. 7 Optical route of two-beam coupling (a); generation of periodic photorefractive grating inside organic photorefractive composites (b); increased orientation enhancement effect in the strengthened built-in electric field by 2D graphitic nanosheets

Fig. 8 Normalized UV–Vis spectra of **ECZ/PC₆₁BM** (a) and **CRA-CSN₇₅-Cz₂₅/ECZ/PC₆₁BM** (b) being undoped/doped by 2D graphitic nanosheets

ECZ/PC₆₁BM. This suggested that 2D graphitic nanosheets have no interaction with **ECZ** and **PC₆₁BM** although the wide absorption characteristics of 2D graphitic nanosheets at the long wavelength are exhibited in the UV–Vis spectrum of nanographite-doped **ECZ/PC₆₁BM**. However, when 2D graphitic nanosheets are doped into **CRA-CSN₇₅-Cz₂₅/ECZ/PC₆₁BM** as shown in Fig. 8b, only the absorption maximum is red-shifted a little and the absorption enhancement at the long wavelength does not appear. This indicated the strong interaction and the energy transfer between 2D graphitic nanosheets and **CRA-CSN₇₅-Cz₂₅** because the absorption maximum around 425 nm comes from the π – π absorptions of photorefractive chromophores. This will also induce the effective trap of photo-generated carriers by the photorefractive compound **CRA-CSN₇₅-Cz₂₅** through the excellent carrier diffusion along the 2D graphitic nanosheets, which is an important issue to strengthen the built-in electric field increasing the orientation enhancement effect in organic photorefractive devices.

When the photorefractive devices fabricated with nanographite-doped **CRA-CSN₇₅-Cz₂₅/ECZ/PC₆₁BM** are placed into the TBC optical route without external electric

field in Fig. 7a, the strong energy exchange between two interfering lights is found as exhibited in Fig. 9a. As depicted in Fig. 9b, the coupling gain coefficient (Γ) in the all-optical operation is firstly increased by nanographite doping. At this time, the doping of 2D graphitic nanosheets only plays a role to improve the diffusion of photo-generated carriers. However, when the nanographite-doping content is more than 0.5 wt%, an evident quenching effect happens because the conductive bridge between electron-rich region and hole-rich region inside the photorefractive grating, being formed hand-by-hand with the further increase in nanographite-doping content, weakens the built-in electric field decreasing the orientation enhancement effect of organic photorefractive chromophores. As a whole, the coupling gain coefficient (Γ) in the all-optical operation is enhanced about 46.4% from 80.1 cm⁻¹ of control device to 117.3 cm⁻¹ of nanographite-doping device due to the excellent conductive characteristics of 2D graphitic nanosheets being less than the size of photorefractive grating period, which indicates that it is an effective and facile approach to improve organic AOC-PR performance for 2D carbonaceous materials to dope organic photorefractive composites.

Fig. 9 TBC signals of nanographite-doped **Cz₂₅/ECZ/PC₆₁BM (a)**; change trend of coupling gain coefficient (Γ) in the all-optical operation with the nanographite-doping contents

4 Conclusion

Two-dimensional (2D) graphitic nanosheets are synthesized by 2D-polymerizing electrophilic and nucleophilic carbon species, to improve organic all-optically controlled photorefractive performance due to their excellent conductive characteristics. Herein, $[\text{C}\equiv\text{C}]^{2-}$ in calcium carbide is applied as nucleophilic carbon species and $[\text{C}(\text{Cl})]$ in carbon tetrachloride (CCl_4) as electrophilic carbon species. When these 2D graphitic nanosheets are doped into organic photorefractive devices, all-optically controlled photorefractive performance without any external electric field is effectively improved because the built-in electric field is strengthened inside organic nanographite-doped photorefractive devices. It is attributed to the effective charge separation under the nonuniform light field caused by the excellent electric conductance of 2D graphitic nanosheets. As a result, the orientation enhancement effect in organic photorefractive devices is strengthened. Finally, the gain coefficient of two-beam coupling in the all-optical operation is enhanced about 46.4% from 80.1 cm^{-1} of control device to 117.2 cm^{-1} of nanographite-doped device. This work provides an effective and facile approach to improve organic all-optically controlled photorefractive performance by 2D graphitic nanosheets.

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Authors' contribution Yingliang Liu designed all the experiments, supervised the ongoing of all the experiments, and prepared the manuscript. Role: Conceptualization, Methodology, Formal analysis and investigation, Writing—original draft preparation, Writing—review and editing, Funding acquisition, Resources, Supervision. Weiwei Zuo synthesized the 2D graphitic nanosheets. Role: Methodology, Formal analysis and investigation. Mingming Li performed all the photorefractive experiments. Role: Methodology, Formal analysis and investigation. Juan Li supplemented and repeated a part of photorefractive experiments. Role: Methodology, Formal analysis and investigation. Shengang Xu and Shaokui Cao supervised the

experimental ongoing and discussed about the experimental results. Role: Resources, Supervision.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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