Strong Two Photon Absorption in BiOBr Nanoflakes

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Abstract: We observe extremely high two photon absorption (TPA) of BiOBr nanoflakes using the Z-scan technique. We report a TPA coefficient as high as $\sim 6.697 \times 10^{-7} \text{ m/W}$ – more than an order of magnitude larger than that of other 2D materials such as graphene and transition metal dichalcogenides.

All-optical signal processing based on nonlinear photonic devices has provided an attractive solution to realize ultrafast signal processing with broad operation bandwidths, low power consumption, and potentially reduced cost [1]. As the material basis for implementing nonlinear photonic devices, advanced materials with superior nonlinear optical properties have been widely investigated [1-7]. Among them, two-dimensional (2D) layered materials such as graphene [2, 3], graphene oxide [4], transition metal dichalcogenides (TMDCs) [5, 6], and black phosphorus (BP) [7] have attracted significant attention. Their remarkable optical properties, such as ultrafast broadband nonlinear optical response including ultrahigh Kerr optical nonlinearity, strong nonlinear absorption, and tunable material properties have already enabled a diverse range of new photonic devices, fundamentally different from those based on traditional bulk materials.

In addition to the 2D materials mentioned above, other novel layered materials have also attracted research interest [8]. Bismuth oxyhalides, i.e., BiOX (X = Cl, Br, I), which consist of $[\text{Bi}_2\text{O}_2]^{2+}$ slabs interleaved by double halogen atoms with weak van der Waals interactions among adjacent slabs of halogen, have been explored as a new group of advanced layered optical materials [8–18]. Recently the improved photocatalytic performance of BiOBr with layer modulation has been reported [9]. High optical nonlinearities of BiOCl layers have also been demonstrated [10, 11].

In this paper, we characterize the nonlinear optical absorption of BiOBr nanoflakes – an important member of the Bismuth oxyhalides (BiOX) family – via the Z-scan technique [19]. Experiment results show that BiOBr nanoflakes exhibit a strong two-photon absorption (TPA - β) of $\sim 6.697 \times 10^{-7} \text{ m/W}$, much higher than typical 2D layered materials such as graphene, TMDCs, and BP. We also characterize the irradiance dependence of the TPA coefficient, demonstrating the strong potential of BiOBr as an advanced nonlinear optical material for high-performance optical limiters to realize pulse shaping, mode locking, and sensor focal-arrays [2].

Figure 1(a) illustrates the atomic structure of BiOBr, where $[\text{Bi}_2\text{O}_2]^{2+}$ slabs are interleaved by double Br atoms to form a layered structure. Such a layered structure enables self-built internal static electric fields and leads to an effective separation of photoinduced electro-hole pairs [8], which is very useful for the enhancement of nonlinear optical absorption [10]. The BiOBr sample used in our experiment was mechanically exfoliated from the bulk crystals onto a glass substrate using adhesive tape. The morphology image and thickness profile of the BiOBr nanoflakes were characterized by the atomic force microscopy (AFM), as shown in Fig. 1(b). The measured thickness of the BiOBr nanoflakes were typically $\sim 75 \text{ nm}$.

Fig. 1. (a) Schematic atomic structure of BiOBr. (b) AFM image of BiOBr nanoflake. (c) Schematic illustration of the Z-scan system.

The third-order nonlinear optical response, including TPA of the prepared BiOBr nanoflakes were measured by the open-aperture (OA) Z-scan setup shown in Fig. 1(c). A Ti:sapphire femtosecond pulsed laser (Coherent, Chameleon) at 800 nm was used to excite the samples. The repetition rate and pulse duration were $\sim 80 \text{ MHz}$ and $\sim 140 \text{ fs}$, respectively. A half-wave plate combined with a linear polarizer was employed as an attenuator to control the input power. The laser beam was focused by an objective (magnification 10 $\times$, numerical aperture 0.25) to achieve a low beam waist of $\sim 2.06 \mu\text{m}$ (Rayleigh range: $\sim 20 \mu\text{m}$) – significantly smaller than the typical flake size. A high-definition CCD imaging system was used to locate the target material and align the transmitted laser to it. In previous reports, the BiOX samples were either dispersed nanoflakes in solution [10] or randomly distributed nanoflakes with nonuniform thicknesses (with a thickness variation $> 100 \text{ nm}$) [11], which could introduce uncontrollable variations in the measured parameters. In contrast, our prepared BiOBr nanoflake

samples had a much more uniform distribution in thickness (variation < 5 nm), which allowed more precise characterization of their optical nonlinearity.

Figure 2(a) shows the measured open aperture (OA) curves of a BiOBr nanoflake at different irradiances, where reverse saturation absorption (RSA) can be clearly observed. Since the photo energy (~ 1.55 eV) of the excitation laser was much smaller than the bandgap of BiOBr (~ 2.73 eV for the bulk and ~ 2.82 eV for the monolayer) [8, 9], yet larger than the half-bandgap, the observed TPA and RSA can be mainly attributed to intensity dependent TPA in the BiOBr nanoflakes. By fitting the OA curves (solid lines in Fig. 2(a)), we obtain a TPA coefficient β as high as $\sim 6.697 \times 10^{-7}$ m/W. In Table 1, we compare the measured β of BiOBr with some other typical 2D layered materials [3, 5–7]. One can see that BiOBr nanoflakes had a β more than an order of magnitude larger than other 2D materials, confirming their superior nonlinear optical absorption property. Finally, as shown in Fig. 2(b), we observe that the β decreased from 6.697×10^{-7} m/W to 6.929×10^{-8} m/W when the laser intensity increased from 0.101 GW/cm² to 1.614 GW/cm², consistent with TPA saturation phenomena reported in other materials [6]. This work highlights the promise of BiOBr for nonlinear optical functions in this wavelength range.

Fig. 2. (a) Measured OA curves of BiOBr nanoflake at different irradiance intensities. (b) Fit β for different irradiance laser intensities.

Table 1. Comparison of TPA coefficient β of various 2D layered materials

Material	Laser parameter	Thickness (nm)	β (m/W)	Reference
Graphene	1150 nm, 100 fs	5-7 layers	3.8×10^{-8}	[3]
WS ₂	1040 nm, 340 fs	57.9	$(1.81 \pm 0.08) \times 10^{-8}$	[5]
MoS ₂	1030 nm, 350 fs	50	$(4.99 \pm 0.02) \times 10^{-9}$	[6]
BP	800 nm, 100 fs	30-60	$(4.5 \pm 0.2) \times 10^{-10}$	[7]
BiOBr	800 nm, 140 fs	75	6.697×10^{-7}	This work

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