Nonlinear saturable absorption of vertically stood WS\textsubscript{2} nanoplates

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We report the nonlinear optical (NLO) properties of vertically stood WS\textsubscript{2} nanoplates excited by 532-nm picosecond laser light. The nanoplates were synthesized by a no-catalyst thermal evaporation process. Raman spectroscopy and x-ray diffraction pattern indicate that the nanoplates are of high crystal quality. The nanoplates exhibit large nonlinear saturable absorption but negligible nonlinear refraction. Mechanisms of the NLO response are proposed. © 2014 Optical Society of America

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Since the discovery of graphene, layered transition metal dichalcogenides (TMDCs) have attracted growing attention, owing to their remarkable electrical and optical properties with intriguing potential in optoelectronic applications \cite{1-4}. Tungsten disulfide (WS\textsubscript{2}) is one of those layered TMDCs. In its bulk form, WS\textsubscript{2} is a semiconductor with direct band-gap of 1.95 eV and indirect band-gap of 2.36 eV \cite{5}. It has been exploited in catalysis, field-effect transistors, lithium ion batteries, and so on \cite{6-9}. But so far, its applicability in photonics and optoelectronics is less studied. As is well known, the development of viable photonic devices primarily depends on materials with remarkable specific optical properties, such as luminescence, optical limiting, and so forth \cite{3,10,11}. Unfortunately, bulk WS\textsubscript{2} crystals or conventionally deposited WS\textsubscript{2} thin films possess no such properties, limiting the range of their use, for instance, in photonics \cite{12,13}.

Bulk WS\textsubscript{2} is composed of covalently bonded S-W-S planes, forming two-dimensional (2D) layers that are bonded together by van der Waals forces, which are weak, allowing the layers to form robust 2D nanostructures similar to graphite nanoclusters. Due to specific 2D confinement of electron motion and an absence of interlayer coupling, single-layer WS\textsubscript{2} possesses a direct band gap, making its light emission dramatically better than that of its bulk counterpart \cite{12,14}. For example, a monolayer WS\textsubscript{2} flake mechanically exfoliated from a synthetic bulk crystal exhibits uniform photoluminescence (PL) \cite{12}. Extraordinary PL near the edge of triangular WS\textsubscript{2} clusters grown by CVD was reported in Ref. \cite{14}. Here, we report our detailed experimental investigation on the ultrafast nonlinear response of WS\textsubscript{2} nanoplates prepared by a no-catalyst thermal evaporation process. To shed more light on the underlying physical mechanisms of their nonlinear optical (NLO) response, experiments were conducted using visible (532 nm) and infrared (1064 nm), picosecond laser pulses at different excitation intensities. In addition, the crystal quality of the WS\textsubscript{2} nanoplates was verified by polarized micro-Raman spectra and compared with the bulk WS\textsubscript{2}.

The WS\textsubscript{2} nanoplate synthesis process was reported elsewhere in detail \cite{15}. Figure 1(a) is a typical image of a large quantity of the WS\textsubscript{2} nanostructures from field-emission scanning electron microscopy (SEM). In the high-magnification SEM image shown in Fig. 1(b), a rod-like feature is observed from the top view because the nanostructures are aligned in a very dense array that is approximately perpendicular to the substrate surface. The array appears to cover the substrate quite uniformly, judging from the SEM images. To determine the

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Fig. 1. (a) Low-magnification and (b) high-magnification SEM images of the nanoplates. The SEM image in the inset (b) was taken under a tilted scan angle. (c) Typical XRD pattern of the WS\textsubscript{2} nanoplates, in which all the diffraction peaks can be assigned to pure 2 H (hexagonal) WS\textsubscript{2}. (d) HRTEM of a single nanoplate.
morphology of the nanostructure, a typical SEM image, taken under a tilted scan angle, of several nanostructures is shown in the inset of Fig. 1(b), clearly displaying a well-defined plate-like morphology of the nanostructure. And it was measured that the width of the plates is in the range of 200–300 nm. By examining tens of the WS$_2$ nanoplates, it was found that their thickness is in the range of 20–30 nm. X-ray diffraction (XRD) patterns of the nanoplates are shown in Fig. 1(c). All the diffraction peaks were indexed to the hexagonal phase of WS$_2$ (2H-WS$_2$). The intense (001) diffraction reveals good crystallinity of the nanoplates, and the high intensity of the (002) diffraction of the $c$ axis reflects the vertical arrangement of the nanoplates. Figure 1(d) is a representative image from high-resolution transmission electron microscopy (HR-TEM), showing a good agreement with the XRD observations [Fig. 1(c)]. The light and dark stripes observed in a single nanoplate confirm its layered structure. The well-resolved periodic lattice fringe, clearly shown in the inset, further reveals the well-crystallized single-crystal nature of these WS$_2$ nanoplates. Based on the measured spacing of dark fringes (about 1.37 nm), the calculated thickness of the nanoplates is approximately 20.49 nm, which is almost equal to the SEM result.

Raman spectroscopy was employed to confirm the atomic structural arrangement of the WS$_2$ nanoplates along with bulk WS$_2$ for comparison under VH and VV polarization configurations, as shown in Fig. 2. Here, VH (VV) means that the incident light is perpendicular (parallel) to the scattered light. The measurement was carried out using a Jobin Yvon HR800 Raman spectrometer with a laser at 532 nm. A typical laser power of 0.1 mW was used in order to avoid sample heating. As previously reported [16–18], the first-order Raman spectra of bulk WS$_2$ in the backscattering geometry show two optical phonon modes ($E_{2g}^1$ at 356 cm$^{-1}$ and $A_{1g}$ at 421 cm$^{-1}$) and one longitudinal acoustic mode (LA(M) at 176 cm$^{-1}$), where $E_{2g}^1$ is an in-plane optical mode and $A_{1g}$ corresponds to the out-of-plane vibrations along the $c$ axis direction of the sulfur atoms. Notably, the $E_{2g}^1$ and $A_{1g}$ peaks are observed in parallel polarization, while only $E_{2g}^1$ peak appears in cross-polarization, similar to the polarization dependence of the corresponding modes in multilayer and bulk MoS$_2$ [19]. Indeed, as determined by the Raman tensors of $E_{2g}^1$ and $A_{1g}$ [19], $E_{2g}^1$ is present in two polarization configurations, while the mode $A_{1g}$ is allowed only under parallel polarization in the backscattering configuration. The peak at 175 cm$^{-1}$ is identified as an LA phonon at the M point, and the broad peak at 351 cm$^{-1}$ is assigned as its second-order phonon 2LA (M) [20]. The other weak peaks at 193, 231, 312, and 324 cm$^{-1}$, labeled by stars ($^*$), are second-order Raman modes [20].

As for the present vertically standing WS$_2$ nanoplates, the positions of all the observed Raman bands are in good agreement with those in bulk WS$_2$, evidencing that the quality levels of both the crystallinity and the lattice are comparable with that of bulk crystal. The new peak at 383 cm$^{-1}$ may be from the multphonon modes at the Brillouin zone edge [20]. The absolute intensity of the main Raman peaks [2LA(M), $E_{2g}^1$, and $A_{1g}$] changes sharply. For example, the $E_{2g}^1$ mode is about 2 times stronger than $A_{1g}$ for bulk WS$_2$, and the $E_{2g}^1$ mode of the nanoplates is overshadowed by the presence of the high-intensity 2LA(M) phonon mode with only half as intense as the $A_{1g}$ mode. Such a behavior could be attributed to a higher scattering volume along $c$ axis of the nanoplates. It must be pointed out that the strong $A_{1g}$ mode is observed in the spectrum of orthorhombic WS$_2$ nanoplates under both VV and VH measurement configurations, showing no obvious dependence on polarization. In principle, for an individual vertically standing WS$_2$ nanoplate, $A_{1g}$ mode is forbidden in cross-(VH) polarization configuration if the polarization direction of the laser is along the $c$ axis. This phenomenon observed in this study is due to the random distribution of the $c$ axis for the investigated WS$_2$ nanoplates. The angle between the polarization direction of the laser and the $c$ axis can be varied from 0 to 90 deg so that $A_{1g}$ phonon can be observed under both VV and VH configurations.

The NLO properties of WS$_2$ nanoplates transferred onto a quartz substrate were investigated by an open-aperture (OA) z-scan system in conjunction with a picosecond Nd:YAG laser operating at 532 nm, 25 ps pulses, with 10 Hz repetition rate. The incident and transmitted laser powers were monitored as the sample was moved (or $z$ scanned) along the propagation direction of laser pulses. Figure 3(a) shows some typical OA z-scans carried out at different incident laser intensities. As shown, the NLO response of WS$_2$ nanoplates took place when the excitation energy was increased to 0.20 GW/cm$^2$. At excitation energies larger than 0.75 GW/cm$^2$, the WS$_2$ nanoplates exhibit a significant saturable absorption (SA) response, similar to that of monolayer and few-layer MoS$_2$ nanosheets for the femtosecond pulses at 800 nm [21]. That is, the total transmission increases with greater intensity of the incident beam, the maximum being at the beam focus.

To quantitatively determine the SA properties of the present WS$_2$ nanoplates, the corresponding Z-scan data were simulated [22]. In the model the optical intensity

![Fig. 2. Raman spectra of bulk WS$_2$ and the present vertically standing WS$_2$ nanoplates under VH and VV configurations, where VH (VV) means that the incident light is perpendicular (parallel) to the scattered light.](image-url)
ZnO nanoplates are promising 2D nanomaterials for optical switches. The authors would like to thank the financial support for this work from the National Natural Science Foundation of China (Grant Nos. 11274052, 51172030, 61274015).
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