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Facile synthesis of two-dimensional WS_2 with reverse saturable absorption and nonlinear refraction properties in the PMMA matrix

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ABSTRACT

We report a versatile, cost-effective and reproducible solid-state reaction approach to synthesize two-dimensional (2D) WS_2 with strong nonlinear optical performances. The reverse saturable absorption and nonlinear refraction properties of 2D WS_2 incorporated into PMMA were measured by the z-scan configuration under femtosecond pulses at 800 nm. The figure of merit and the nonlinear optical refractive index n_2 were calculated to be ~0.40 × 10^{-13} esu cm and ~3.34 × 10^{-4} cm^2/GW, respectively. Furthermore, optical limiting (OL) effects of the WS_2/PMMA composite were observed with OL threshold F_{OL} ~2.4 mJ/cm^2, which is lower than those of previously reported OL materials. Such results imply the WS_2/PMMA composite as a potential candidate for practical OL applications and the solid-state reaction technology provides a feasible approach for the preparation of 2D WS_2 applied in the field of nanophotonics.

1. Introduction

Along with the significant developments of powerful pulsed lasers and related technologies, lasers have been widely applied in the fields of medicine, scientific research, entertainment, electronics, industries and military [1–6]. However, the potential damage of laser to sensitive instruments and human eyes was exposed, and this has motivated the development of functional materials for laser protection. Optical limiting (OL) materials, which effectively block high intensity light but allow low intensity pass, can be expected to meet the requirements of the efficient laser protection [6–8]. Many materials including carbon-based materials [9], metal nanoparticles [10,11] and graphene [5] in solutions, have been extensively studied for their OL effects. The main reason for the OL behavior of these materials is associated with the nonlinear scattering, owing to the formation of solvent microbubbles. However, due to the bubble-formation time needing several nanoseconds (ns), OL products for femtosecond (fs) or picosecond (ps) laser pulse is less common than those for ns laser pulse. And liquid OL materials are indeed not suitable for practical applications and device integration. Such materials inevitably suffer from agglomeration when store for a long time, leading to deterioration of OL effect. Hence, it strongly stimulates us to seek OL solid materials for fs or ps laser pulse. π-Conjugated organic molecules [12], other aromatic molecules and graphene [1,2] display OL behavior for fs laser pulse because of strong multiphoton absorption or excited-state absorption. However, the OL thresholds of these OL materials are relatively high. Very recently, transition metal disulfides (TMDs: WS_2, MoS_2, etc.), as one of the graphene analogue, have attracted a great deal of attention [13–19]. Due to the energy band gap of TMDs changing from the indirect to direct band as reducing the number of layers, a series of exotic photonic properties emerge in few-layer TMDs, which cannot be observed in the bulk TMDs. Several research groups demonstrated strong OL performances in few-layer TMDs and few-layer TMDs–composites for ps or ns laser pulse [6,20]. The fs OL effect with very low threshold of WS_2 (or other TMDs) solid material has not yet been reported so far.

On the other hand, similar to graphene, the preparation of two-dimensional (2D) WS_2 has also ignited great attention from the scientific community to realize a wide range of applications. Among the various methods to construct 2D WS_2, chemical vapor deposition (CVD) [13], sulfurization of tungsten oxide films [21] and

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liquid-phased exfoliation [22] are the most common approaches. However, CVD and sulfurization of tungsten oxide films techniques inherently lack flexibility, because of a high temperature, an expensive set up, complicated and dangerous. Also, some additives are usually added for the liquid-phased exfoliation method, and this probably changes the intrinsic physical performances of WS_2. What's more, the high-yielded production of 2D WS_2 is still highly challenging.

On the basis of the above key factors, we report the solid-state reaction technology for synthesizing high-yielded 2D WS_2. This method is very convenient, cost-effective, reproducible, and less detrimental to the intrinsic physical performances of 2D WS_2 due to the lack of any additives. Transmission electron microscopy (TEM), Raman spectrum, absorption spectrum and photoluminescence (PL) spectrum proved that the 2D WS_2 were successfully prepared. The as-synthesized 2D WS_2 were incorporated into polymethylmethacrylate (PMMA) to generate the solid composite material. Under fs laser excitation at 800 nm, the WS_2/PMMA composite exhibited OL property and nonlinear refraction response, identified by z-scan experimental setup. The high figure of merit, large nonlinear optical (NLO) refractive index and large third-order NLO susceptibility were obtained. Furthermore, OL effects with very low threshold were also observed, the OL threshold of the WS_2/PMMA composite is lower than those of previously reported OL materials. These results demonstrate that the WS_2/PMMA composite is very promising for application in optical limiter and the solid-state reaction offers a feasible approach for the fabrication of 2D materials applied in nanophotonic devices.

2. Experimental details

2.1. Preparation of 2D WS_2

Raw materials of 0.3221 g tungsten trioxide (WO_3, Sigma-Aldrich) and 3.1750 g thiourea (NH_2CSNH_2, Sigma-Aldrich) were first mixed homogeneously in an agate mortar, then fired in a covered corundum crucible at 790 °C for 1 h under the atmosphere of nitrogen. The resulting sample was cooled down to room temperature and 0.3371 g black WS_2 was collected. Then, the WS_2 powders were dispersed in ethyl alcohol under mild stirring to form a yellow-green solution. To remove large agglomeration, the WS_2 dispersions were centrifuged at 3000 rpm for 15 min, and the upper supernatant was collected to incorporate into PMMA. 10 mL methyl methacrylate (MMA) and WS_2 suspension were mixed and heated at 75 °C for 10 min, then 0.0115 g benzoyl peroxide (BPO) was added and heated at 75 °C for another 10 min, followed by heat treatment at 105 °C for 25 min. Finally, it was kept at 75 °C for 30 h and solid transparent WS_2/PMMA was obtained. The incorporated WS_2 concentration in WS_2/PMMA is about 0.0068 mg/cm^3.

2.2. Material characterization

X-ray diffraction (XRD) pattern was performed on a Philips X'Pert Pro Super diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) radiation. Microstructure was characterized by a JEM-2010 TEM (JOEL Ltd., Tokyo, Japan). Raman spectrum was recorded using a Raman spectrometer (RenishawinVia, Gloucestershire, UK) and a 785 nm laser as the excitation source. Optical absorption spectrum was measured on a Perkin-Elmer Lambda-900 Ultraviolet/Visible/Near-infrared (UV/vis/NIR) spectrophotometer (Perkin Elmer, Waltham, MA). A PL spectrum was measured on a FS920 fluorescence spectrophotometer (Edinburgh, U.K.) equipped with a 450-W Xenon lamp. The NLO properties of the sample were measured using a commercial Ti: sapphire fs laser (center wavelength $\lambda = 800$ nm, pulse width $t_p = 130$ fs and 1 kHz repetition rate). In order to more precisely identify the measured data, CS_2 solution contained in a cuvette (1 mm in thick) was used to calibrate. All the measurements were carried out at room temperature.

3. Results and discussion

XRD technique was performed on sample to study the structural information. As plotted in Fig. 1(a), it clearly shows that all the diffraction peaks agree quite well with the standard hexagonal 2H-WS_2 structure (JCPDS Card No. 87-2417), in which the diffraction peaks at $2\theta = 13.9$, 28.2, 32.8, 33.3, 39.3, 58.2 and 68.7° can be unambiguously assigned to the (002), (004), (100), (101), (103), (110) and (200) planes, respectively. No apparent peaks from the impurity phase are observed, and the sharp diffraction peaks imply a good crystallinity of the obtained WS_2.

A typical low-magnification TEM image in Fig. 1(b) visualizes that high-yielded 2D WS_2 were successfully synthesized by means of a facile solid-state reaction method. We can ascertain the layer number of layered material from high-resolution (HRTEM) image of the folded edge [23]. As directly evidenced from Fig. 1(c), the 2D WS_2 mainly contain 5 sandwiched S-W-S layers, corresponding to the thickness of the as-synthesized 2D WS_2 less than 4 nm. HRTEM image shows that the interlayer distance of (002) crystal plane of the 2D WS_2 is about 0.630 nm. Moreover, HRTEM image also evidently exhibits the lattice fringes with a spacing of 0.274 nm, which is congruent with $d = 0.273$ nm of the (100) planes of hexagonal WS_2. In addition, from TEM and HRTEM images, clear ripples and corrugations can be observed, manifesting the ultrathin nature of the obtained 2D WS_2 [23,24]. Selected area electron diffraction (SAED) pattern in Fig. 1(d) reveals that the as-prepared 2D WS_2 is polycrystal, which is composed of several few-layers single-crystal WS_2 stacked in different orientations.

An optical absorption spectrum of the 2D WS_2 dispersions was depicted in Fig. 2(a). Note that three characteristic absorption bands located at 400–700 nm regions are in good agreement with the general features of few-layers WS_2 with hexagonal symmetry, suggesting that the 2D WS_2 were dispersed in ethyl alcohol as the 2H-phase. The dual peaks which result from the inter-band excitonic transition at the K point, known as the B and A transitions, respectively, around 525 (~2.361 eV) and 626 nm (~1.980 eV) in accordance with the previous studies on the 2D WS_2 [25,26]. The energy difference between the B and A peaks, which is an indication of the strength of spin-orbit interaction, is approximately 381 meV in reasonable agreement with the calculations [26]. It is worth mentioning that the average thickness of the as-prepared WS_2 also can be deduced to be less than ~4 nm from the A exciton position. Such a phenomenon confirms that the ultrathin 2D WS_2 were successfully obtained. Besides, the weak absorption band at 449 nm, labeled transition C in the Yoffe study, is also observed, which arises from the optical transition between the density of states in the valence band and conduction band at the Q point in the 2D Brillouin Zone [27–29]. Inset shows the characteristic yellow-green color of the WS_2 dispersions in ethyl alcohol, similar to that in other reports [3]. In order to avoid agglomeration when idle for a long time, exclude the influence of nonlinear scattering (NLS) mainly caused by the microbubble formation and realize various optical applications such as saturable absorber, optical limiter and so on, the 2D WS_2 have been incorporated into PMMA, the well known organic optical glass. Fig. 2(b) shows the absorption spectrum of the WS_2/PMMA composite bulk material, the characteristic absorption bands between 400 and 700 nm corresponding to the WS_2 dispersions in ethyl alcohol are also observed. It means that the intrinsic properties of 2D WS_2 have not been changed in incorporation process. The homogeneous yellow-green color of the inset of Fig. 2(b) reveals that the 2D WS_2 have