Flexible engineering of light emission in monolayer MoS$_2$ via direct laser writing for multimode optical recording

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ABSTRACT
Direct laser writing has been proved to be capable for effective modulation of optical and electrical properties of various nanomaterials. In this work, we designed a flexible direct laser writing approach to engineer photoluminescence (PL) properties of monolayer MoS$_2$ and present its potential application in optical recording. PL spectra evolution of monolayer MoS$_2$ under continuous-wave laser writing has been explored, where its PL energy can be precisely controlled by changing the writing time. This feature enables a multimode optical recording with spectral contrast in monolayer limit materials for high-capacity data storage technologies. Here, we constructed a proof-of-principle multimode optical recording on monolayer MoS$_2$ based on the PL wavelength division multiplexing scheme and discussed the relevant challenges for practical applications. Our flexible approach with a mask-free feature and high spatial resolution is promising for applications in two-dimensional material-based information storage and optoelectronic devices.

I. INTRODUCTION
Direct laser writing has been used widely for producing micrometer-sized features and three-dimensional (3D) microdevices due to its advantages of nanometer spatial resolution, maskless lithography, and 3D prototyping capability. By utilizing this technique, the optical and electrical properties of many nanomaterials, including carbon nanotubes, gold nanorods, and graphene oxide, have been modified effectively and controllably. This kind of flexible tunability provides a promising route in developing high-capacity optical data storage. For example, a multilevel optical index modulation accompanied by a fluorescence intensity change in graphene oxide was determined through direct laser writing, enabling 3D holographic images, multimode optical recordings, and laser patterning of complex 3D structures. In particular, a five-dimensional optical recording scheme with a promising disk capacity of 7.23 Tbyte has been explored by Gu and co-workers through direct laser writing on gold nanorods based on its photothermal recording mechanism.

Very recently, direct laser writing on layered MoS$_2$, the representative two-dimensional (2D) transition metal dichalcogenides (TMDs), has been investigated experimentally as well. Through direct laser writing, Lili and co-workers demonstrated laser thinning and patterning with layer-by-layer precision in MoS$_2$. Furthermore, Sow and co-workers reported that an improved performance of MoS$_2$-based photodetectors could be obtained via direct patterning ultrathin MoS$_2$ films. Moreover, the patterning of periodic ripples in monolayer MoS$_2$ was manifested by Kim et al., based on the mismatch of the thermal expansion between the substrate and MoS$_2$. Although some functional microstructures on layered MoS$_2$
have been constructed and applied to fabricate high-performance optoelectronic devices, the utilization of the unique optical features of monolayer MoS$_2$ by direct laser writing, especially its potential applications in multimode optical recording, has not been explored.

In this work, we designed a facile and effective direct laser writing approach to controllably modify the optical properties of monolayer MoS$_2$. By changing the writing time, photoluminescence (PL) spectra of monolayer MoS$_2$ can be precisely modulated from 1770 meV to 1822 meV. Given this modification, we presented a proof-of-principle spectral encoding optical storage based on the wavelength division multiplexing (WDM) scheme. In comparison with the optical storage based on integrated PL intensity, which is strongly dependent on the reading power, the peak energy of the PL spectrum is robust and almost insensitive to the reading power, opening a promising way of optical data storage through spectral encoding.

II. EXPERIMENTAL DETAILS

Monolayer MoS$_2$, purchased from SixCarbon Technology Shenzhen, was synthesized on the SiO$_2$/Si substrate by chemical vapor deposition (CVD). The quality of the prepared samples has been characterized by optical and atomic force microscopy (Fig. S1).

All the experiments, including direct laser writing, PL imaging, and spectra measurements, were performed by using a home-built scanning confocal microscope, and the schematic diagram has been provided in the supplementary material (Fig. S2). A continuous-wave (CW) 532 nm laser was used for both writing and reading the optical recording. The power of the writing laser, which was used to engineer the PL spectra of MoS$_2$ and encode the desired information, was generally set to 10 mW. Here, the reading laser was used to decode the recording information. To avoid further engineering during the reading process, the power of the reading laser should be much lower than that of the writing power. Hence, the power of the reading laser was usually set to about 0.1 mW. By using a dry objective (100×, 0.9NA), the laser was tightly focused on the sample surface. MoS$_2$ was placed on a motorized three-dimensional piezoelectric ceramic stage. Optical recording was achieved by moving the MoS$_2$ sample with respect to the focused laser beam in a programmable way.

III. RESULTS AND DISCUSSION

PL engineering on monolayer MoS$_2$ by direct laser writing has been investigated by some groups, and the relevant mechanisms have also been discussed in our previous studies. However, the repeatability of engineering is still unsatisfactory, which...
mainly results from the rather different qualities (the defect density) of the monolayer materials. By investigating dozens of monolayer MoS$_2$ prepared by CVD methods, we found that the PL intensity and spectra of several samples can be well controlled by changing the writing time, as shown in Figs. 1(a) and 1(b), respectively. Figure 1(c) presents the normalized PL spectra as a function of writing time, which displays an unexpectedly significant and regular blue shift in PL energies, varying from 1770 meV to 1822 meV. The precision control of PL energies is highly desirable for optoelectronic applications. These spectral profiles can be well deconvoluted into two components, as shown in Fig. 1(d). According to the previous studies, $^{22,25}$ the two components can be attributed to neutral exciton (A$_0$) and charged exciton (trion, A$_T$), respectively. The energy difference between the two peaks in the region of 30 meV–50 meV [at the bottom of Fig. 1(e)], coinciding with the trion dissociation energy reported in the relevant works, $^{22,26}$ further confirms our assignment. We also analyzed the excitation-power-dependent PL spectra, as shown in Fig. S3. The sublinear features indicate defect-related nonradiative recombination paths. This result also suggests that the fruitful engineering on the PL spectra of monolayer MoS$_2$ can be attributed to the laser-induced defects and the subsequent adsorption of gas molecules. Laser-induced defects generally increase monotonically with the growth of writing time, resulting in the accumulation of gas molecules (such as O$_2$ and H$_2$O) adsorbed on or bonded to these new-formed defects. According to the previous investigations, $^{22,22}$ these gas molecules will deplete the excess electrons, leading to the conversion from A$_T$ to A$_0$ (Fig. S4). This conversion gives rise to the enhancement of integrated PL intensity and the blue shift in PL spectra, while further writing will ultimately damage the monolayer materials, resulting in a decrease in PL intensity. To prove the role of gas molecules, we performed a control experiment, where the sample was placed in a vacuum chamber. PL evolutions of MoS$_2$ under medium (0.26 atm) and high ($8 \times 10^{-4}$ atm) vacuum conditions and a pure N$_2$ atmosphere are presented in Fig. 1(f). Note that PL intensity rapidly quenched in all cases. We can straightforwardly attribute the phenomenon to the absence of O$_2$ and H$_2$O. Furthermore, a small peak can be found in the medium vacuum, more or less similar to that shown in Fig. 1(a). On the other aspect, PL evolutions under high vacuum and N$_2$ conditions are also similar (although a very weak PL enhancement can be found, possibly resulting from the residual O$_2$ or H$_2$O). These results further confirm the role of O$_2$ and H$_2$O.

The precision control of PL spectra via direct laser writing opens a promising way for optical data storage through the wavelength division multiplexing (WDM) scheme. As we know, bandwidth and channel spacing are critical parameters for storage capacity. In this work, the bandwidth is 52 meV (from 1770 meV to 1822 meV), and the channel spacing depends on the stability or
the error of PL spectra under laser engineering. The main error of our scheme originates from the inhomogeneous quality of monolayer MoS$_2$ as well as the engineering process. To explore the error of the engineering process, we measured PL spectra of hundreds of engineered spots on neighboring monolayer MoS$_2$ flakes and performed spectral analysis to determine the peak energy distributions of $A^0$ and $A^T$ for each spot. The determined parameters of engineered spots after direct laser writing (with a power of 10 mW and a time of 360 s) are presented in Fig. 2(a). We can find that the histograms of $A^0$, $A^T$, and the weight-average peak of ~300 engineered spots basically present the Gauss normal distribution, where the center values and the standard deviations (3σ) are $1846.3 \pm 6.6$ meV, $1801.3 \pm 7.5$ meV, and $1820.8 \pm 6.9$ meV, respectively. After careful consideration, we use the averaged peaks under four engineered levels [the writing times of which are 0 s ($t_1$), 120 s ($t_2$), 200 s ($t_3$), and 360 s ($t_4$), respectively] to encode information, as shown in Fig. 2(b). The central values and the corresponding deviations (3σ) of averaged peaks under these four conditions are $1770.0 \pm 7.8$ meV ($t_1$), $1782.8 \pm 9.3$ meV ($t_2$), $1803.7 \pm 10.8$ meV ($t_3$), and $1820.8 \pm 6.9$ meV ($t_4$), respectively. Consequently, the energy region of the four WDM channels are set to $E_{c1} \leq 1775.8$ meV, $1775.8$ meV $< E_{c2} \leq 1792.5$ meV, $1792.5$ meV $< E_{c3} \leq 1814.2$, and $E_{c4} > 1814.2$ meV, respectively.

Finally, a proof-of-principle spectral encoding optical storage was performed on a triangle monolayer MoS$_2$, as shown in Figs. 2(c) and 2(d). 15 spots have been written with four levels through the scheme mentioned above. PL spectra of these spots have been studied (Fig. S5) and analyzed, and their peak energies have been labeled in Fig. 2(e). Although the PL energies under each engineered level (highlighted by four different colors) show a little fluctuation, most of the values are still loaded in the region of each designed channel ($E_{c1}$ to $E_{c4}$). Therefore, the four channels can be applicable for recording multimode information. To further clarify the multimode, we re-encode the information into two binary sets, as illustrated in Fig. 2(f). Consequently, we show that the WDM scheme provides excellent potential to develop high-density optical data storage. Further improvement in data capacity is warranted if we can heighten the control precision of PL spectra, thus reducing the error of engineering and subsequently decreasing the channel spacing. In this case, many more WDM channels are available. On the other hand, the atomic thickness of MoS$_2$ is the thinnest optical storage medium. By producing multi-stacked monolayer MoS$_2$ films with thin transparent spacers (such as SiO$_2$), an ultra-high-capacity can be accessed.

As mentioned above, along with the engineering of PL spectra, PL intensity was also modified, as shown in Fig. 1(a). The result proves that integrated PL intensity can be used as the parameter to record information as well. However, this approach is greatly sensitive to the reading power, which will affect the accuracy of information storage when the reading power is changed or even fluctuates. Figure 3(a) presents the spectral profiles of eight individual spots after writing with the same conditions (10 mW and 360 s) while reading with three different powers, which were 0.08 mW, 0.1 mW, and 0.12 mW, respectively. The integrated time of PL spectra was all 10 s. We can find that integrated PL intensities of these spots are significantly different, as presented in Fig. 3(b). The difference

![Image](image-url)

**FIG. 3.** Comparison of PL peaks and integrated intensity at different reading powers: PL spectra (a) and their normalizations (c) of eight individual spots written by 532 nm at a power of 10 mW and a time of 360 s. Three different powers ($P_1$, 0.08 mW; $P_2$, 0.1 mW; and $P_3$, 0.12 mW) were used to read the PL spectra and integrated PL intensities (b) and their peak energies (d) of the engineered spots. The shadow in d represents the 3σ standard deviations of the fourth engineering level ($1820.8 \pm 6.9$ meV).
mainly results from the variation in reading power. In contrast, the difference in their PL spectra is negligible, as shown in Fig. 3(c). The determined peak energies entirely lie in the distribution of the fourth level [Fig. 3(d)]. The robust recording based on the contrast of PL spectra with a reading-power-insensitive feature enables high information fidelity and security.

Although a multimode optical encoding on monolayer MoS$_2$ by direct laser writing has been demonstrated, many challenges remain for its practical application. First, the peak energy of monolayer MoS$_2$ sensitive to defect density and the surrounding environments must be precisely manipulated to reduce the error rates [a bit error occurs, as shown in Fig. 2(f)]. This obstacle can be partially solved by monitoring the spectral profiles of the engineered spots during the writing process, rather than measuring and analyzing the spectra after writing. Another challenge of optical data storage is its low writing speed and limited storage capacity. An ultrahigh-repetition-rate laser with high pulse energy may present an answer to improve the access speed. However, a clear solution is still elusive. The spatial resolution was about 3 $\mu$m in this experiment, limited by the thermal diffusion effect during the writing process. This obstacle may be overcome by using a femtosecond laser with a two-photon scheme, which has a tight focus on both lateral and axial directions. Combining the high resolution in the lateral direction and the multi-stacked monolayer in the axial direction, as well as the WDM scheme, a high capacity is prospective. A rewritable scheme is also an important target. Very recently, we achieved reversible PL engineering on monolayer MoS$_2$ by switching the gas atmosphere, which has also been reported by Ardekani and co-workers. In particular, we determined an all-optical reversible manipulation of PL emission in monolayer WS$_2$ without changing the gas environment. These results offer enlightening ideas for rewritable optical storage on layered TMD materials. Furthermore, the accurate recording must be writing, storing, and reading under the same atmospheric condition due to the sensitivity of PL spectra to the gas molecules. Fortunately, we have proved that the recording still survives for more than three years by just storing the engineered samples in a clean air condition.

**IV. CONCLUSION**

In conclusion, we have proposed a flexible direct laser writing approach to engineer PL properties of monolayer MoS$_2$ and presented its promising applications in multimode optical recording. Both PL intensity and spectra of monolayer MoS$_2$ can be well controlled by changing the writing time of the direct laser writing approach. Based on the precise control of PL spectra, a WDM scheme has been carried out to achieve a multimode optical recording. Although some challenges to practical applications still remain, we believe that direct laser writing on layered TMD materials has excellent potential for high-capacity information technologies and flexible micro-photonic devices.

**SUPPLEMENTARY MATERIAL**

See the supplementary material for characterizations, optical setup, excitation-power-dependent PL spectra, spectral weight of $A^0$ and $A^+$ as a function of writing time, and PL spectra of 15 written spots.

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**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**REFERENCES**


