Approaching the ultrathin-film absorption limit with monolayer semiconductor superlattices

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Abstract: Strongly absorbing materials are needed for nanoscale photonics and optoelectronics, including strong light-matter coupling applications. The absorption of ultrathin films in a symmetric optical environment is fundamentally limited to 50%. The strong excitonic resonance in monolayer WS₂ provides 16% absorptance. Here, we demonstrate that monolayer WS₂ superlattices provide higher absorption while preserving the exciton emission. We show that an artificial superlattice structure increases absorptance to 31%. Our results put forward superlattices as a platform for developing novel two-dimensional semiconductor devices.

Keywords: monolayer semiconductors; heterostructures; superlattices; molecular doping.

Introduction

Strong light absorption in ultrathin materials plays a vital role in variety of applications including light detection, waveguiding, and modulation. Atomically thin semiconductors are a relatively new class of strongly absorbing materials. Transition metal dichalcogenides (TMDs), such as tungsten disulfide (WS₂) and molybdenum diselenide (MoSe₂) possess unique optical properties. Bulk TMDs consist of weakly bound atomically thin layers and stable monolayers can be easily prepared through exfoliation. Compared to other growth methods such as chemical vapor deposition (CVD), exfoliation provides the highest exciton quality for the strongest absorption and narrowest linewidth [1].

Monolayer TMDs, despite being less than one nanometer thick, show an exceptionally strong absorption of light; absorption of sunlight up to 5-10% has been observed in a TMD monolayer, an order of magnitude larger than GaAs or Si of comparable thickness [2]. The strong interaction of light with TMDs monolayers has potential advantages in atomically thin devices. The combination of strong absorption and the ability to tune the excitonic resonances through doping enables their use in nanoscale optical elements such as atomically thin photodetectors [3], modulators [4], and lenses [5]. TMD monolayers can also be used to create atomically thin mirrors that are promising for a range of uses, including spatial light modulators, active metasurfaces, and active cavity control [6]. In addition, the high oscillator strengths and sharp resonances of excitons in these materials can enable reaching the regime of strong light-matter coupling and the manipulation of light via surface exciton-polaritons [7], [8].

Here, we create WS₂ monolayer-based structures to approach the fundamental thin-film absorption limit of 50%. We demonstrate three simple methods to obtain stronger
absorption than a monolayer WS₂. Different superlattice structures of WS₂ monolayers result in an increased light absorption, while also preserving the exciton emission and quality (Figure 1a). We characterize these structures using transmission and photoluminescence spectroscopy. Additionally, we employ hyperspectral imaging to gain insight into the spatial variations of exciton properties. Our work puts forward the potential of monolayer superlattices as a flexible platform for developing novel two-dimensional nanophotonic devices. As the superlattice fabrication process relies on simple methods, such superabsorber materials are posed to have an impact on a variety of devices.

**Results**

We start with simple structures containing two monolayers separated by a spacer to retain the optical properties of the individual monolayers. Such artificial bilayers provide a basis for higher-order superlattices structure to approach the absorption limit. The weak van der Waals interaction between the layers creates a spacer filled with air and impurities during fabrication. Compared to a monolayer, we demonstrate an increase in transmission contrast to ~30% (Figure 1b). In addition, the PL intensity of the artificial bilayer approximately doubles compared to the monolayer case, attributed to the absence of interlayer coupling, allowing the maintenance and preservation of exciton emission and quality. The absorption increase is accompanied by only a slight increase in linewidth with a small redshift is observed, likely influenced by the higher permittivity in the surroundings due to the presence of the other monolayer, the additional PDMS superstrate, or impurities introduced in the stamping process. However, such structures prove to have coupling between layers that is difficult to control reliably and results in absorption reduction. We observe this coupling when applying heating or storing the sample in vacuum, which reveal a significant impact on the interaction between layers. As a more reliable and reproducible spacer, we demonstrate the use of an organic molecular spacer to construct stable, stacked bilayers. In our molecular-spacer heterostructures, we utilized 7,7,8,8-tetracyanoquinodimethane (TCNQ, Ossila Ltd) as p-type doping molecules. A concentration of 1 mM was prepared by dissolving 4.1 mg of TCNQ powder in 20 mL of methanol. The solution (20 µL) was then pipetted onto a WS₂ monolayer on a PDMS/glass substrate and spin-cast for 1 minute at 500 rpm to achieve a thin and uniform film with minimal damage to the monolayer semiconductor. This molecular spacer bilayer demonstrates notable light absorption of approximately 27%. In addition, we managed to achieve a 1.5-fold increase in the PL intensity of the bilayer compared to the monolayer (Figure 1c).
Figure 1 | Stacking of monolayers WS\textsubscript{2} into superlattices provides higher absorption while preserving the exciton emission. \textbf{a,} Approaches for artificial stacking of WS\textsubscript{2} monolayers with a spacer for reaching the ultra-thin film absorption limit. \textbf{b,} Comparison of transmittance contrast between monolayer WS\textsubscript{2} (black) and an assembled bilayer with an air spacer in a symmetrical PDMS environment, highlighting the higher contrast in the artificial bilayer (red). Inset: photoluminescence (PL) map illustrating the pronounced luminescence of the artificial bilayer. \textbf{c,} Transmittance, and PL spectra of a bilayer WS\textsubscript{2} with a controlled molecular spacer, achieved using a TCNQ concentration of 1 mM. The molecular spacer bilayer demonstrates enhanced absorption and PL intensity compared to the monolayer.

Achieving scalability for a thicker superlattice poses challenges, particularly in the case of the molecular spacer, due to the yield limitations of the transfer technique. Therefore, we fabricate higher-order superlattices with an increased number of layers using Al\textsubscript{2}O\textsubscript{3} as a thin dielectric spacer deposited using atomic layer deposition to approach the thin-film absorption limit in a more scalable process. Compared to the monolayers within the structure, a WS\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} superlattice with four monolayers boosts the optical absorptance to \(~31\%\) (Figures 2a and 2b). We also observed an increase in PL as we add more layers. However, the increase in PL peak is not consistent for extra layers due to the accumulation of defects during ALD deposition and the impurities throughout the stamping process (Figure 2a).
**Conclusion**

Our study shows that stacking WS$_2$ monolayers in superlattice structures boosts absorption and maintains exciton emission quality. Introducing an artificial bilayer increased absorption to over 25% but controlling spacer thickness remains a challenge. Using TCNQ molecules as a molecular spacer proved effective, offering controllable thickness, and additionally acting as a beneficial $p$-type dopant for WS$_2$. Furthermore, constructing a WS$_2$/Al$_2$O$_3$ superlattice with four monolayers achieved optical absorption of approximately 31%. Superlattice structures, versatile in enhancing exciton properties and improving absorption, hold thus significant potential for optimizing the optical properties of TMDs for nanoscale photonic and optoelectronic devices.

**References**


