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Bulk monolayer: Bring monolayer optical nonlinearity into solution-processible bulk films

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Monolayer transition metal dichalcogenides have high nonlinear optical susceptibility but are limited by atomic thickness. Zhou et al. found that MoS_2 superlattice thin films enhance second harmonic generation efficiency, retaining nonlinear susceptibilities and offering tunable optical cross sections for improved light-matter interaction.

Second harmonic generation (SHG) is a nonlinear frequency conversion process where two photons with the same fundamental wavelength are converted into a single SHG photon with half the wavelength. As the most prototypical nonlinear optical (NLO) process, SHG plays a significant role in laser techniques for expanding wavelength ranges while also enabling quantum states of light, with essential applications in ultrafast lasers.[1] The advancement of SHG techniques relies on the development of novel NLO crystals. Two-dimensional (2D) monolayer molybdenum disulfide (MoS_2) possesses a large second-order NLO susceptibility ($\chi^{(2)}$) that is two orders of magnitude higher than conventional NLO crystals such as beta-barium borate.[2] Additionally, it is well suited for heterogeneous on-chip integration, making it a promising material candidate for next-generation NLO devices.

However, the antiparallel layer stacking in the naturally existing 2H-phase MoS_2 preserves inversion symmetry, resulting in suppressed SHG. As a result, SHG is only observed in the monolayer limit and vanishes in the 2H bulk crystals, which inevitably limits the optical cross section for light-matter interaction and severely compromises SHG performance. Therefore, to leverage the merit of monolayer MoS_2 for SHG, it is crucial to achieve a tunable thickness (optical depth) while maintaining the monolayer NLO properties. Different from 2H-MoS_2, each atomic layer in rhombohedral MoS_2 (3R-MoS_2) is stacked in parallel, satisfying the inversion symmetry breaking required for SHG.[3] Moreover, quasi-phase matching can be achieved by twisting the interlayer-thick crystals at a specific angle, further boosting the SHG efficiency.[4] Nevertheless, the scalable growth of pure 3R-MoS_2 large-area thin films is still challenging, and layer twisting relies on arduous layer-by-layer transfer. Recently, a new class of monolayer atomic crystal molecular superlattice has emerged, featuring alternating layers of monolayer atomic crystals and organic molecules,[5–7] yet there has been very limited exploration in the field of nonlinear optics.

In a recently published *Matter* paper,[8] Zhou et al. reported a solution-processible method to produce large-area MoS_2 thin films, preserving noncentrosymmetry to enable highly efficient SHG. Superlattice containing MoS_2 2D atomic crystals and poly(vinylpyrrolidone) (PVP) organic layers can be created by re-assembling the exfoliated monolayers with surface functionalization of PVP ligands using spin- or spray-coating techniques (Figure 1A). PVP is an insulating polymer with a highest occupied molecular orbital-lowest unoccupied molecular orbital energy gap much larger than the visible range, which can be regarded as a passive optical material that effectively isolates MoS_2 interlayer coupling, preserving monolayer MoS_2 properties with a direct electronic band gap and strong excitonic resonance. Additionally, the inversion symmetry is naturally broken due to the presence of PVP spacers and the random assembly process. Consequently, the superior monolayer optical properties can be well preserved in such multilayered organic hybrid superlattice thin films, which can be referred to as "bulk monolayer" MoS_2 (BM-MoS_2). Fabry-Perot cavity resonance can be attained by tuning the thickness of BM-MoS_2, resulting in a giant SHG enhancement (Figures 1A and 1B). Remarkably, the SHG from a ~30-nm-thick BM-MoS_2 film exhibited a 126-fold enhancement compared with that of monolayer MoS_2 (Figure 1C) and a nearly infinite enhancement compared with pristine bulk 2H-phase MoS_2, which showed negligible SHG signal due to inversion symmetry restoration. Furthermore, the SHG intensity of BM-MoS_2 was 21 times stronger than that of a single-crystal gallium arsenide (GaAs) wafer, a well-characterized benchmark material known for having large SHG susceptibilities among known semiconductors.[9] Theoretical calculations further explored the influence of organic layer properties on the SHG performance of BM-MoS_2, emphasizing that the construction of BM-MoS_2 thin films with ultrathin organic layers and a low refractive index is crucial for achieving enhanced SHG.

This study introduces a facile strategy in the scalable fabrication of area- and thickness-scalable bulk monolayer 2D thin films that retain the intrinsic

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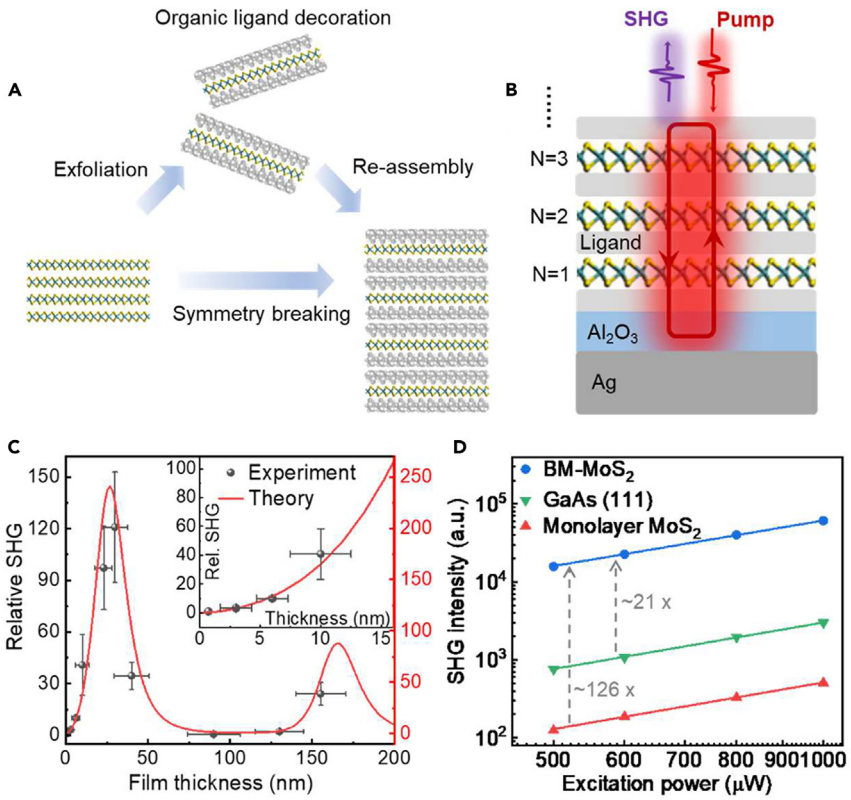

Figure 1. BM-MoS_2 thin film structure and SHG

(A) Schematics of BM-MoS_2 thin film preparation.

(B) Schematics of SHG enhancement induced by the extended interaction between BM-MoS_2 and the pumping light.

(C) Thickness-dependent SHG of BM-MoS_2.

(D) Excitation power-dependent SHG of a BM-MoS_2 thin film in comparison with monolayer MoS_2 and GaAs single-crystalline wafer.

physical properties of monolayer crystals. In particular, the authors have shown that their bulk monolayer materials possess the exceptionally large NLO susceptibility of monolayer atomic crystals and tunable optical depth for light-matter interactions, creating an attractive NLO material for various coherent frequency conversion processes beyond SHG, including high-order harmonic generation, four-wave mixing, sum, and difference frequency generation. Similar to monolayer transition metal dichalcogenides (TMDs), NLO generation in bulk monolayer TMDs may be effectively modulated by tuning the excitonic resonance conditions, enabling electrical control of NLO devices through electrostatic gating. In addition to the insulating PVP molecule in this study, integrating optically active organic semiconductors with strong electronic coupling to TMDs into bulk monolayer materials is also of great interest, as it can achieve a synergetic optical response. The integration of such optically active materials could realize a vast parameter space to further tailor light-matter interactions. Furthermore, bulk monolayer thin films can be readily integrated into versatile optical components such as optical fibers, metasurfaces, and ring resonators, opening new avenues for the development of on-chip photonic devices.

DECLARATION OF INTERESTS

The author declares no competing interests.

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