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Waved 2D Transition-Metal Disulfides for Nanodevices and Catalysis: A First-Principle Study

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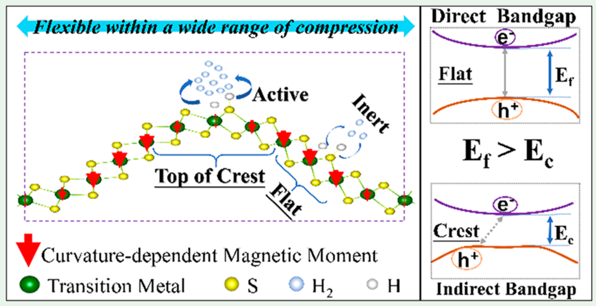
ABSTRACT: Two-dimensional (2D) transition-metal dichalcogenides (TMDs) monolayers have found various applications spanning from electronics in physics to catalysis in chemistry due to their unique physical and chemical properties. Here, the effect of structure engineering on the physical and chemical properties of transition-metal disulfide monolayers (MS_2) is systematically investigated based on density functional theory (DFT) calculations. The calculation results show that waved MS_2 (w-MS_2) can be achieved under compression due to the zero in-plane stiffness, leading to high flexibility within a wide range of compression. The bandgap and conductivity of semiconducting w-MS_2 are reduced because the d orbitals of transition-metal elements become more localized as the curvature increases. A transition from a direct band to an indirect one is observed in w-MoS_2 and w-WS_2 after a critical strain. We further demonstrate the structure engineering can modulate the magnetism of w-VS_2, leading to nonuniform distribution of magnetic moments along the curvature. Furthermore, we find that waved TMDs show reduced Gibbs free energy for hydrogen adsorption, resulting in enhanced catalytic performance in hydrogen reaction evolution (HER). It is expected that the waved 2D TMDs may find applications into various areas, such as nanodevices and catalysis.



KEYWORDS: *waved 2D materials, transition-metal disulfides, strain engineering, electronic and magnetic properties, hydrogen evolution reaction, DFT calculations*

■ INTRODUCTION

Since the discovery of graphene in 2004, two-dimensional (2D) materials have triggered extensive interests in many research fields due to their excellent physical and chemical properties.[1−4] Their intriguing properties have resulted in wide applications in various areas, such as mechanics,[5,6] electronics,[7,8] photoelectronics,[9,10] and catalysts.[11,12] Among them, transition-metal dichalcogenides (TMDs) have attracted increasing attention because of their versatile and tunable properties.[13] Different from graphene, the TMD monolayer is a three-layer structure (X-M-X: M = transition metal atom, and X = chalcogen atom), which provides a lot of chances to tailor their properties for multiple applications. Various methods, such as electron and atom doping,[14,15] vacancy control,[16] deformation,[17] and thermal annealing,[18] have been used for the purpose, and amazing properties have been reported, such as valley electronics,[19] magnetism,[20] and superconductivity.[21]

The out-of-plane deformation, such as buckling,[22] wrinkling,[23] scrolling,[24] and folding,[25] is observed in many 2D materials because of their ultrathin nature, which has triggered greatly attention recently.[26,27] For instance, waved graphene had been reported to show high performance on molecule adsorption, chemical reaction, and hydrogen evolution reaction (HER).[28−33] Xie et al. reported that a spontaneous ripple superlattice was formed when a van der Waals (vdW) TMD heterostructure with large lattice mismatch was fabricated.[34] Out-of-plane deformation (or bended structure) has also been reported on other 2D TMDs.[35,36] However, to the best of our knowledge, few systematic studies have reported on their physical and chemical properties affected by the periodic curvatures. In this work, we construct waved MS_2 (M = Mo, W, Sn, and V) to investigate the effect of curvature on their physical and chemical properties using first-principles calculations. We find that these waved nanosheets show high flexibility upon compression, and their band structures depend on the compression, resulting in a transition from direct bandgap to an indirect one. The compression has no effect on the ground states of waved MS_2 but strongly affects the local magnetic moments (LMM) of magnetic w-VS_2, leading to the nonuniform distribution of magnetic moments along the curvature. We further show that the curvature can improve the catalytic activity of MS_2 for HER, which is greatly enhanced by simply increasing the compression. Our well-rounded calcu-

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