

## Moiré metal for catalysis

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(Received 21 February 2022; accepted 27 June 2024; published 29 July 2024)

The search for highly efficient and low-cost catalysts based on earth abundant elements is one of the main driving forces in organic and inorganic chemistry. In this work, we introduce the concept of moiré metal for hydrogen evolution reaction (HER). Using twisted NbS<sub>2</sub> as an example, we show that the spatially varying interlayer coupling leads to a corresponding variation of Gibbs free energy for hydrogen absorption at different sites on the moiré superlattice. Remarkably, as a HER catalyst, twisted NbS<sub>2</sub> is shown to cover the thermoneutral volcano peak, exceeding the efficiency of the current record platinum. The richness of local chemical environment in moiré structures provides a versatile method for designing superior catalysts.

DOI: [10.1103/PhysRevB.110.L041407](https://doi.org/10.1103/PhysRevB.110.L041407)

Heterogeneous catalysis [1,2] plays a key role in chemical and medical industries by enabling large-scale production and selective product formation. Currently, the production of 90% of chemicals (by volume) is assisted by solid catalysts. An important chemical reaction for the supply of “green energy” is to produce hydrogen (H<sub>2</sub>) from water using thermal, solar, or electric energy. In particular, the electrochemical generation of hydrogen molecules, known as hydrogen evolution reaction (HER), has the advantage of high reaction speed and eco-friendliness. The key component of electrochemical reaction system is electrocatalysts with high intrinsic reactivity and long-term stability. For the industry-level applications, the rational design of low-cost electrocatalysts based on earth abundant elements is in high demand.

The hydrogen electrocatalytic reaction speed is known to correlate with the intrinsic properties of solid catalysts. Various descriptors, such as d-band center, d-band charge, pH values, bond length, active site density, etc., have been introduced to predict the tendency of the electrocatalytic reactivities [3–5]. Beyond these empirical descriptors, the most quantitative intrinsic figure of merit for HER catalyst is the Gibbs free energy [ $\Delta G(H)$ ] of hydrogen absorption [6,7] at the equilibrium potential. To now, the most efficient electrocatalysts for HER are Pt-group metals, as Pt and Pd have  $\Delta G(H)$  close to the ideal HER volcano diagram peak  $\Delta G(H) = 0$  eV.

Metal catalysts rely on the surface dangling bonds as the active sites for chemical absorption. In industry, solid catalysts are often porous or dispersed on a supporting material to maximize surface area and enhance catalytic reactivity. However, for bulk materials, the active catalytic surface area-to-mass ratio is still quite limited. Recently, atomic thin van der Waals (vdW) materials have been studied for catalysis [8–17] due to the maximized surface/volume ratio, potentially enabling “all surface reaction.” The calculations of  $\Delta G(H)$  of vdW materials within the basal plane show that the best catalyst is monolayer TMD NbS<sub>2</sub> with  $\Delta G(H) = 0.31$  eV [10], which still falls far behind Pt/Pd in terms of reactivity.

In this work, we propose a new method to enhance chemical reactivity under a broad range of environmental conditions using vdW metals with moiré structures. Such “moiré metals” can be created by stacking two layers of identical vdW metals with a twist angle [18,19] or two different layers with a lattice mismatch. Our key idea is that in a moiré superlattice, the spatial variation of stacking configuration produces a corresponding variation of Gibbs free energy for hydrogen absorption in different local regions. Such variation of  $\Delta G(H)$  enables the self-adaptive optimization of chemisorption property for a wide range of reaction environments.

Using first-principles calculations, we further identify the twisted AB stacked NbS<sub>2</sub> as the superior catalyst with highest reactivity for HER compared to elementary metals and topological metals. At intermediate twist angle  $\theta = 5.08^\circ$ , a 150-meV range of Gibbs free energy for hydrogen adsorption at different locations in the basal plane is observed, covering the  $\Delta G(H) = 0$  eV HER volcano diagram peak for standard reaction environment.

To reveal the origin of the spatial variation of  $\Delta G(H)$ , we calculate stacking-dependent band structures and find that interlayer coupling varies significantly. By developing a simple tight-binding model, we present a heuristic argument that the spatially varying interlayer coupling on the moiré superlattice is responsible for the variation of  $\Delta G(H)$  found in our large-scale DFT calculation.

Presently, semiconductor based moiré materials have been intensively studied in the physics community [20], such as twisted bilayer graphene [18,19] and group-VI semiconductor TMD heterostructures [21–37]. Here, for the purpose of catalysis, we consider moiré metals formed by stacking two layers of group-V metallic TMDs MX<sub>2</sub> in 2H structure, such as NbSe<sub>2</sub> and NbS<sub>2</sub>. In the case of homobilayers with a small twist angle  $\theta$  (relative to the natural bilayer stacking), the moiré superlattice, shown in Fig. 3, has a superlattice constant  $a_M = a_b/\sqrt{\delta^2 + \theta^2}$ , where  $\delta = (a_b - a_t)/a_t$ , with  $a_b(a_t)$  the lattice constant of each layer. In this superlattice, there are three high symmetry regions denoted as MM, XX, and MX;

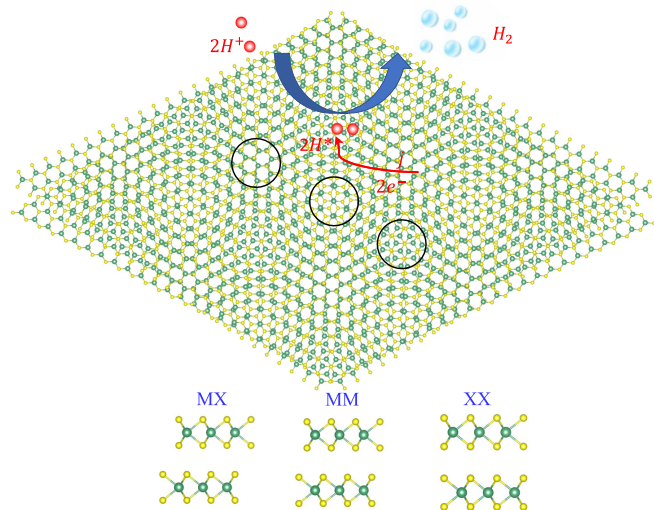


FIG. 1. Schematic of HER process at three high-symmetry stacking regions of 2H TMDs, where two protons and two electrons from electrode are combined to form a hydrogen molecule. The tuning of HER catalytic properties in the bilayer vdW metals are related to the local d-band center shift [5] and bandwidth at different stacking regions. We circle MX, MM, and XX regions in moiré superlattice from left to right direction and present the enlarged side view of three regions at lower panel.

see Fig. 1. In MX region, the M atom on the bottom layer is locally aligned with the X atom on the top layer, as in natural TMD bilayers. On the other hand, in the MM (or XX) region, the M (or X) atoms on both layers are locally aligned. Importantly, MM and XX stacking configurations are thermodynamically unstable and made possible only by moiré engineering.

We calculate the electronic structures of bilayer NbS<sub>2</sub> for different stacking configurations. Monolayer NbS<sub>2</sub> features with three electron pockets near *K*, *K'*, and  $\Gamma$  valleys, and the half-filled conduction bands are entirely formed from *d* orbitals of Nb atom. As shown in Fig. 2, the  $\Gamma$  valley in bilayers exhibits a large bonding-antibonding splitting on the order of 0.5 eV due to vdW interlayer coupling. Importantly, this bilayer splitting varies significantly depending on the layer stacking: 0.6 eV for MM, 0.5 eV for MX, and 0.46 eV for XX. The underlying variation in interlayer coupling is due to different distances between adjacent metallic atoms on the two layers.

In twisted NbS<sub>2</sub> moiré superlattice, the spatial variation of interlayer coupling in different local regions provides a variety of local charging environments for the chemisorption of hydrogen atoms and molecules. The surface hydrogen binding energy directly determines its hydrogen production speed. The HER process involves hydrogen absorption and desorption as shown in Fig. 1. Initially, the Volmer reaction transfers one electron to a proton to form an adsorbed hydrogen atom on the surface of catalyst ( $H^+ + e^- + * \rightarrow H^*$ , where \* denotes the active catalyst and  $H^*$  is the intermediate). Next, the desorption of  $H_2$  can be achieved by either Tafel reaction ( $2H^* \rightarrow H_2 + 2*$ ) or Heyrovsky reaction ( $H^+ + e^- + H^* \rightarrow H_2 + *$ ).

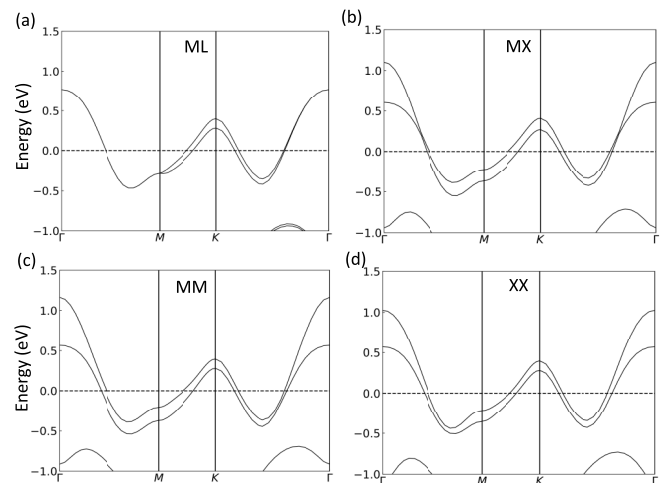


FIG. 2. DFT band structure of (a) monolayer, (b) MX stacked bilayer (natural stacking), (c) MM stacked bilayer, and (d) XX stacked NbS<sub>2</sub> with antiparallel orientation. The interlayer coupling has a large variation at different stacking regions as seen in the corresponding  $\Gamma$  pockets splitting.

Therefore, under the standard electrochemical reaction condition (room temperature and atmospheric pressure), the overall HER reaction rate is largely determined by the binding energy ( $\Delta E_H$ ) of the intermediate  $H^*$  and the density of the active sites in the catalyst. A strong bonding between hydrogen atom and catalyst slows down the desorption step (Heyrovsky or Tafel), while a weak bonding slows down the adsorption step (Volmer reaction). A direct descriptor for reaction speed is Gibbs free energy for hydrogen absorption, defined as  $\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T\Delta S$ , with  $\Delta E_{ZPE}$  and  $\Delta S$  as the difference in zero-point energy and entropy between the adsorbed species and the gas molecule, respectively. Hereafter we use the value  $\Delta E_{ZPE} - T\Delta S = 0.3$  eV for standard electrochemical reaction condition. The ideal reaction rate is achieved at thermoneutral condition when  $\Delta G_H \sim 0$  eV [38].

To investigate  $\Delta G(H)$  for moiré metal, we first calculate the electronic structure of twisted bilayer NbS<sub>2</sub> with angle  $\theta = 5.08^\circ$ . To obtain fully relaxed lattice structures, we perform large-scale density functional theory calculations with the SCAN+rVV10 van der Waals density functional [42], which captures the intermediate-range van der Waals interaction through its semilocal exchange term, resulting in a better estimation of layer spacing. Owing to the different local atomic arrangements in the MM, XX, and MX regions, the layer distance is found to have a strong spatial variation as shown in the supplementary material, which are 6.14, 6.11, and 6.39 Å for the MM, MX, and XX regions in  $\theta = 5.08^\circ$  AB stacked moiré superlattices, respectively. The twisting significantly modified the density of states compared to the natural MX stacked bilayer, and the density of states peak has a shift of 100 meV. Plotting the charge density for states from  $E_f - 0.5$  eV to  $E_f$  ( $E_f$  is the Fermi level), we find the out of plane distributions are quite different at three moiré regions, and XX region is more spread out than others.

In the twisted AB stacked NbS<sub>2</sub> with angle  $\theta = 5.08^\circ$ , we calculate Gibbs free energy for hydrogen adsorption at

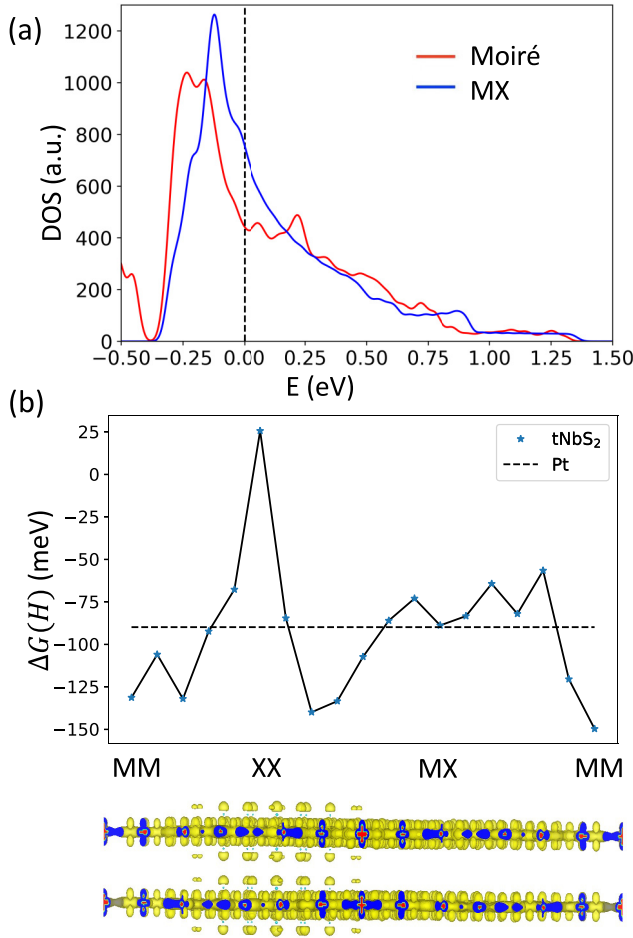


FIG. 3. (a) Comparison of density of states for natural stacking MX and moiré superlattice. The density of states near Fermi level is significantly modified by twisting. (b) Upper panel is the Gibbs free energy diagram for hydrogen evolution under standard conditions (1 bar of  $H_2$  and pH = 0 at 300 K). Energies of the intermediate states are calculated using the SCAN+rVV10 vdW functional as described in the Methods. Coverage of one hydrogen atom per moiré superlattice is used for all calculations. Lower panel is the wave-function plot for twisted  $NbS_2$  between  $E_f - 0.5$  eV to  $E_f$  along the MM, XX, and MX path. The wave function is more spread out at the XX region.

the basal plane, especially for the line connecting three high-symmetry stacking regions as shown in Fig. 3(a).  $\Delta G(H)$  is obtained as  $\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T \Delta S$ . Here  $\Delta E_H$  is the hydrogen binding energy which was calculated as  $\Delta E_H = E(\text{moiré} + H) - E(\text{moiré}) - 1/2E(H_2)$  for one hydrogen atom per moiré superlattice. The  $E(\text{moiré} + H)$ ,  $E(\text{moiré})$ , and  $E(H_2)$  are the total energy of respective parts.

Remarkably, the spatially dependent  $\Delta G(H)$  in the basal plane covers the  $\Delta G(H) = 0$  eV. At XX region, which is thermodynamically inaccessible without twisting, we find a Gibbs free energy  $\Delta G(H) = 0.01$  eV. At MM region with largest interlayer coupling, the  $\Delta G(H)$  is  $-0.13$  eV, lower than the natural stacking region MX with  $\Delta G(H) = -0.09$  eV. In the line plot across three high-symmetry stacking regions as shown in Fig. 3(d), we find half of the basal plane sites have absolute reactivity comparable or better than platinum.

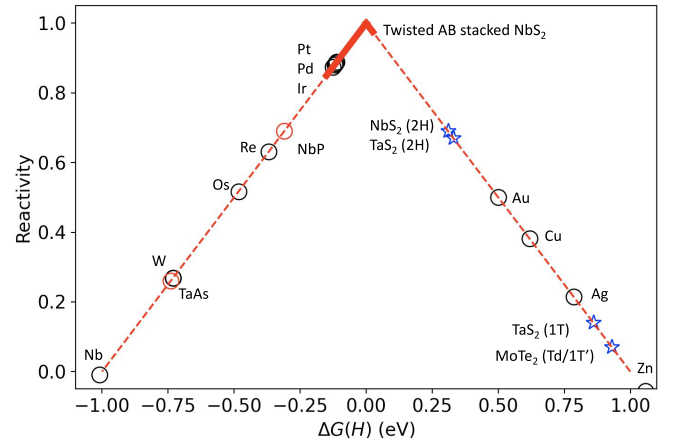


FIG. 4. Predicted relative activities of various HER catalysts following the volcano scheme as a function of calculated Gibbs free energy of hydrogen adsorption on the surface of the catalyst. Circle stands for elemental metals and topological metals, star stands for vdW metals at basal plane. The Gibbs free energy data for untwisted metal is collected from the previous literature [10,39–41].

In the volcano-shaped diagram shown in Fig. 4, we collect the Gibbs free energy for hydrogen adsorption of the twisted vdW metal  $NbS_2$  with a variety of single metals, topological metals, and two-dimensional (2D) materials collected from the literature [6,43]. Among all studied bulk materials for HER catalysis, Pt with a Gibbs free energy  $\Delta G(H) = -0.09$  eV is the most efficient electrocatalyst thus far and used in industry despite the high material cost. A recent experiment on doped bulk  $NbS_2$  demonstrates the ultrahigh-current-density for hydrogen evolution, which is close to platinum [44]. Unlike the limited types of catalytic sites in conventional bulk or vdW materials, moiré engineering provides a wide and adjustable range of hydrogen absorption energies for the HER process in various environments with different pressure, temperature, and hydrogen potentials. Importantly, the AB-stacked bilayer  $NbS_2$  at  $\theta = 5.08^\circ$  covers the volcano peak, providing a superior HER catalyst over all known materials at equilibrium potential.

To gain insight into the origin of the stacking-dependent hydrogen binding energy, we consider a simplified tight-binding model for a twisted bilayer metal, including nearest-neighbor intralayer and interlayer hopping:

$$t_{xy}(\mathbf{d}) = t_1 \left( \frac{\mathbf{d} \cdot \hat{\mathbf{z}}}{d} \right)^2; \quad t_z(\mathbf{d}) = t_2 \left( \frac{1 - \mathbf{d} \cdot \hat{\mathbf{z}}}{d} \right)^2. \quad (1)$$

Herein  $t_1 = t_1^0 e^{-(r-a)/\delta_1}$ ,  $t_2 = t_2^0 e^{-(r-d_c)/\delta_2}$ , and  $a = 3.34$  Å,  $d = 6.12$  Å is the in-plane lattice constant and layer distance of MM stacked region, intralayer hopping  $t_1^0 = 0.184$  eV is fitted to match the DFT calculated density of states of  $\Gamma$  pocket,  $t_2^0 = 0.30$  eV is determined by the band splitting at  $\Gamma$  of MM stacking configuration, the scaling parameters  $\delta_1 = 0.3$  Å and  $\delta_2 = 1.1$  Å are determined from total energy of tight binding model.

To calculate the total energy for hydrogen atoms adsorbed at the basal plane, we introduce one hydrogen atom attached to the sulfur site with constant onsite potential and hopping

energy. The onsite energy of hydrogen atom is set to be  $V_H = 0.45$  eV relative to that of Nb atoms. We fit the hopping from hydrogen to Nb atom as  $t_H = 2.45$  eV by matching the DFT calculated density of states ( $\Gamma$  pocket Fermi surface) in MM stacked region. Although our model is greatly simplified, it correctly captures the binding energy variation across the high-symmetry stacking regions: MM, MX, and XX. We plot the Gibbs free energy in the same manner as the large-scale DFT calculation shown in Supplemental Material [45]. The tight-binding description captures the overall energy scale quite well, and shows a good agreement for enlarged  $\Delta G(H)$  of XX and MM region compared to MX region, which are  $-96$ ,  $-50$ , and  $1$  meV, respectively.

The dependence of chemical adsorption on local stacking configuration in moiré metals can be directly probed by scanning tunneling microscopy (STM). Previous STM studies have directly imaged adsorbed hydrogen atoms on the surface of conventional metals [46]. For moiré metal, we expect that the spatially varying surface-hydrogen bond strength leads to an inhomogeneous hydrogen density distribution that correlates with the local stacking variation.

While we have focused on the twisted homobilayer NbS<sub>2</sub> as a prime example of moiré metals, similar stacking-dependent chemisorption is expected in heterobilayers such as NbSe<sub>2</sub>/NbS<sub>2</sub>. The powerful chemical vapor deposition [47] method enables the scalable preparation of high-quality and low-cost 2D heterostructures towards the real-world application of moiré metal catalysts. Besides HER, we also expect the moiré engineering for metals can optimize the chemisorption of the alkali metal ions for the design of electrode materials and nitrogen and oxygen atoms for the catalysis of small organic molecules and oxygen reduction reaction. The chiral nature of moiré superlattices further provide a unique way towards heterogeneous asymmetric catalysis.

In conclusion, we have shown that the moiré engineering strongly enhances the HER reactivity of vdW metals due to the spatially varying interlayer bonding strength. We have identified twisted NbS<sub>2</sub> as the ideal catalyst for the  $H_2$  evolution reaction, covering the volcano peak  $\Delta G(H) = 0$  eV. Our work provides a guiding principle for the design of highly efficient and low-cost HER catalysts from the emerging field of artificial moiré materials. In a broad sense, the moiré engineering of surface chemical properties provides a physical way for the rational design of superior electrocatalysts for a variety of chemical reactions under different environmental conditions, with the aim of closing the carbon, hydrogen, and nitrogen cycle with renewable electricity.

*Method.* We performed the density functional calculations using generalized gradient approximation [48] with SCAN+rVV10 van der Waals density functional [42] as implemented in the Vienna Ab initio Simulation Package [49]. Pseudopotentials are used to describe the electron-ion interactions. We first construct AA and AB stacked NbS<sub>2</sub>/NbS<sub>2</sub> homobilayer with vacuum spacing larger than 20 Å to avoid artificial interaction between the periodic images along the  $z$  direction. Dipole correction is added to the local potential in order to correct the errors introduced by the periodic boundary conditions in the out-of-plane direction. The structure relaxation is performed with force on each atom less than 0.01 eV/Å. We use Gamma-point sampling for structure relaxation and self-consistent calculations, due to the large moiré unit cell.

We acknowledge Yan Sun, Guowei Li, Jinfeng Jia, Vidya Madhavan, and Eva Andrei for valuable discussions and comments on the paper. This work was supported by Simons Investigator award from the Simons Foundation and CIFAR Catalyst Fund.

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