Among transition metal dichalcogenides (TMdCs) as alternatives for Pt-based catalysts, metallic-TMdCs catalysts have highly reactive basal-plane but are unstable. Meanwhile, chemically stable semiconducting-TMdCs show limiting catalytic activity due to their inactive basal-plane. Here, metallic vanadium sulfide (VS$_2$) nanodispersed in a semiconducting MoS$_2$ film (V–MoS$_2$) is proposed as an efficient catalyst. During synthesis, vanadium atoms are substituted into hexagonal monolayer MoS$_2$ to form randomly distributed VS$_n$ units. The V–MoS$_2$ film on a Cu electrode exhibits Pt-scalable catalytic performance; current density of 1000 mA cm$^{-2}$ at 0.6 V and overpotential of $-0.08$ V at a current density of 10 mA cm$^{-2}$ with excellent cycle stability for hydrogen-evolution-reaction (HER). The high intrinsic HER performance of V–MoS$_2$ is explained by the efficient electron transfer from the Cu electrode to chalcogen vacancies near vanadium sites with optimal Gibbs free energy ($-0.02$ eV). This study provides insight into ways to engineer TMdCs at the atomic-level to boost intrinsic catalytic activity for hydrogen evolution.

One renewable energy resource is water electrolysis for hydrogen production. Noble metals such as Pt and Pd as catalysts for water electrolysis are inevitably utilized for efficient hydrogen evolution,[1–3] which have been limited for industry application owing to scarcity and high cost. Therefore, it is highly desired to develop efficient noble-metal free catalyst. Among a variety of noble-metal free catalysts, transition metal dichalcogenide (TMdC)-layered material has been proposed. Metallic TMdCs such as VS$_2$,[4] VSe$_2$,[5] and NbS$_2$[6] demonstrate great potential for hydrogen-evolution-reaction (HER) performance owing to their active basal plane and high electrical conductivity but are often not stable in air,[7–9] and most importantly in HER environment,[5,10] which is a primary concern for industrial targets. Meanwhile, semiconducting TMdCs such as MoS$_2$ and WS$_2$ in monolayer form[11–13] are stable in air but are inactive in the basal plane and have poor electrical conductivity. Additionally, monolayer TMdCs allow for short electron injection paths from the electrode to active sites to promote efficient HER performance, unlike the bulk materials, which offers limited HER kinetics because of charge lagging to reach active surface sites.[14,15]

Several approaches with semiconducting TMdCs have been investigated to resolve the basal-plane inactivity including chalcogen vacancies, phase boundaries, and heterostructures.[16–18] Although the hydrogen adsorption Gibbs free energy ($\Delta G_{H^+}$) approaches nearly zero in chalcogen vacancies and heterostructures, electrical conductivity remains poor, leaving sluggish HER kinetics.[14,15,18] Heterophase boundaries are highly reactive in terms of HER but the necessary phase-boundary line density is rarely encountered.[17] Structural transformation from the semiconducting 2H-phase to metallic...
1T phase renders these materials reactive with respect to HER performance but unfavorable owing to the thermodynamically unstable 1T phase.[19] Recently, the substitution of metal and chalcogen atoms in bulk s-TMDCs prepared by hydrothermal method improved the HER performance, but the complicated structures make it difficult to understand the underlying HER mechanism.[20–22] Our research target is to take advantage of the highly conductive basal plane of monolayer TMDc film in large-area for efficient HER performance, yet to obtain a material with high stability. Here, we construct a one-step chemical vapor deposition (CVD) process to directly synthesize metallic vanadium sulfide (VS₄) units nanodispersed in semiconducting monolayer MoS₂ film (V–MoS₂) and further demonstrate superb HER performance via overpotential, hydrogen turnover frequency (TOF), cycle test, and Gibbs free energy that are comparable to those of Pt catalyst.

Figure 1a depicts the ball-and-stick model for randomly dispersed VS₄ unit in the active basal plane of a hexagonal MoS₂ monolayer. Most importantly, the chalcogen vacancy is created near the vanadium site, which is defined as a VS₄ unit. This unit plays an important role as active sites in the basal plane to promote both efficient charge transfer and hydrogen adsorption. The nanodispersed VS₄ units in monolayer MoS₂ film was synthesized by one-step CVD process (see Experimental Section and Figure S1, Supporting Information). Atomic structures and the homogeneity of V distribution in V–MoS₂ at 9.3 at% V concentration are provided in an annular dark field scanning transmission electron microscopy (ADF-STEM) image (Figure 1b and Figures S2 and S3, Supporting Information). We note that the bright contrast features are frequently observed on top of the samples in the ADF-STEM images. This is confirmed from the poly(methyl methacrylate) (PMMA) residues introduced for transfer of the samples, but not from the presence of V clusters (Figures S4–S6, Supporting Information). The d-spacing between S–S in the VS₄ unit, which is confirmed by observing the (1010) plane from the electron diffraction pattern shown in the inset, is 0.27 nm, similar to that of pristine 2H-MoS₂ (0.27 nm).[23] The real and simulated ADF-STEM images (the square region in Figure 1b) show the atomic configuration of the VS₄ unit region with an S vacancy in V–MoS₂ (Figure 1c). Furthermore, the intensity profile clearly distinguishes among Mo, S, and V atoms and the S vacancy next to the V atom (V-vac) (Figure 1d and inset: top view of the atomic configuration). These results indicate that the V atoms are well-substituted into Mo sites in the 2H–MoS₂ lattice with negligible strains. The formation of VS₄ units was readily confirmed by newly emerged peak in Raman spectra and reduced photoluminescence intensity due to the enhanced metallic character (Figure S1, Supporting Information). The presence of V atoms in the as-grown V–MoS₂ film was additionally confirmed by energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy (Figures S7–S9, Supporting Information).

We carefully analyzed the atomic configurations of V at the Mo site (VMo), V-vac, Mo at the Mo site (MoMo), the S vacancy next to the Mo atom (Mo-vac), and the S dimer (2S) (Figure 1e and Figure S10, Supporting Information). Interestingly, the amount of V-vac is proportional to the VMo concentration, the molar ratio of V to the Mo precursor (Figure 1f and Figures S11–S15, Supporting Information) for more details), with a similar trend to that of the longitudinal acoustic mode phonon in Raman spectra originating from impurity levels[24] (Figure S16, Supporting Information). The coverage of monolayer region reaches up to 95% (5% multilayer region) in V₀.93Mo₀.07S₂ (Figures S17 and S18, Supporting Information). Meanwhile, the amount of Mo-vac in V–MoS₂ is stochastically populated up to 2.1%, regardless of VMo amount (Figure 1f). The higher V-vac amount of ≈22.0% per V atom than Mo-Vac amount of 1.2% per Mo atom is congruent with our theoretical calculations, where the formation energy of V-vac is 0.22 eV more stable than that of Mo-vac (Table S1, Supporting Information). The ample VMo and V-vac sites are the key ingredient for efficient electron transfer and hydrogen adsorption, which will be discussed later.

Figure 2a shows the polarization curves in the linear sweep voltammetry plot with varying V concentration and substrate (see Experimental Section for a detailed description of the measurements). Ni and Cu electrodes were chosen for their earth abundance and relatively high electrical conductivities in comparison with conventional graphite (Gr). The polarization curve of V–MoS₂ with the Gr substrate shifts to the Pt curve with increasing V concentration, surpassing that of pristine MoS₂. The overpotential with the Ni substrate is further reduced relative to that with the Gr substrate (Figure 2b). It is remarkable to see that with the Cu substrate, V–MoS₂ shows a similar overpotential in low current density region to that of Pt.

The overpotential for 10 mA cm⁻² (ɳ₀) for assessing catalytic efficiency are extracted from linear sweep voltammetry plot.[25] The overpotential gradually decreases to ~0.19 V in V₀.93Mo₀.07S₂ with the Gr substrate (Figure 2b). The ɳ₀ is further improved by using a different substrate. In particular, V₀.93Mo₀.07S₂ with the Cu substrate demonstrates the lowest ɳ₀ (~0.08 V) and a hydrogen TOF of 0.3 s⁻¹ at 0 V (Figure 2c), comparable to those of Pt[26] (ɳ₀ of ~0.04 V and TOF of 0.7 s⁻¹). Furthermore, the current density reaches to 1000 mA cm⁻² at 0.6 V, which is viable in industrial requirements (Figure S19, Supporting Information). The outstanding onset potential and ɳ₀ of V₀.93Mo₀.07S₂ are further compared with those of other 2D materials (Figure S20, Supporting Information).

To evaluate the stability in HER environment, we perform chronoamperometry measurements and an accelerated degradation test. The V₀.93Mo₀.07S₂ sample clearly demonstrates no significant drop in the current density at different current densities of 1, 10, and 50 mA cm⁻² for 24 h (Figure 2d). Additionally, the polarization curves are fully superimposed after 5000 cycles, regardless of the substrate used (Figure 2e). Also, the chemical shifts, the change of morphology, and physical structure before and after cycling were negligible (X-ray photoelectron spectroscopy, scanning electron microscopy (SEM), and Raman analysis in Figure S21, Supporting Information). This superb stability is crucial to meet industrial target and is well-contrasted with that of pure metallic VS₂.[4]

To investigate the origin of the charge transfer kinetics and catalytically active sites in V–MoS₂, we measured the charge-transfer resistance (Rₓ) and double-layer capacitance (Cdl) by using impedance spectroscopy and cyclic voltammetry, respectively (see Experimental Section and Figures S22–S25, Supporting Information). The Rₓ rapidly drops at the minute concentration of 0.8 at% V from that of pristine MoS₂ and gradually reduces to saturate at a concentration of 9.3 at% V (Figure 2f). Such a drastic reduction in Rₓ is ascribed to the degenerate metallic VS₂ of
the high concentration of 9.3 at% V in the semiconducting MoS$_2$ lattice.[27] The $R_{ct}$ for V$_{0.390}$–MoS$_2$/Cu is reduced to 0.8 Ω, which is the lowest $R_{ct}$ value ever recorded for a 2D monolayer TMdC electrocatalyst to date, and even lower than that of Pt (2.2 Ω) (Figure S22, Supporting Information). The electrochemically active surface area (EASA) extracted from the $C_d$[28] is nearly negligible for pristine MoS$_2$, compared to that of Gr (Figure S25 and Table S2. Supporting Information). This value is gradually elevated with the V concentration, reaching to 28.2 mF cm$^{-2}$ for V$_{0.390}$–MoS$_2$, twice as high as that of pristine MoS$_2$ (13.2 mF cm$^{-2}$). The EASA with the Cu substrate in V$_{0.390}$–MoS$_2$ is further improved from the Gr substrate, ensuring the importance of substrate for industrial applications. Furthermore, EASA normalized polarization curves demonstrate outstanding HER performance of
Figure 2. HER activity of V–MoS$_2$ in terms of V concentration and substrate. a) Polarization curves for pristine MoS$_2$ on graphite (Gr) substrate, V$_{(0.8\%)}$–MoS$_2$/Gr, V$_{(1.6\%)}$–MoS$_2$/Gr, V$_{(7.3\%)}$–MoS$_2$/Gr, V$_{(9.3\%)}$–MoS$_2$/Ni, V$_{(9.3\%)}$–MoS$_2$/Cu, and Pt measured in N$_2$ saturated 0.5 M H$_2$SO$_4$ electrolyte at 25 °C at a scan rate of 5 mV s$^{-1}$. b) Overpotential at 10 mA cm$^{-2}$ ($\eta_{10}$) of V–MoS$_2$ samples. c) Turnover frequency of V$_{(9.3\%)}$–MoS$_2$/Cu compared to pristine MoS$_2$. d) Chronoamperometric curves of V$_{(9.3\%)}$–MoS$_2$/Gr under static current densities of 1, 10, and 50 mA cm$^{-2}$ for 24 h. e) Accelerated degradation test of V$_{(9.3\%)}$–MoS$_2$/Gr, Cu, and Ni substrates after 5000 CV cycles. f) Charge transfer resistance ($R_{ct}$) and double layer capacitance ($C_{dl}$) of V–MoS$_2$ samples as a function of V concentration. The substrate dependence on Gr, Ni, and Cu at V$_{(9.3\%)}$–MoS$_2$.

V–MoS$_2$/Cu as compared to other materials (Figure S26 and Table S3, Supporting Information). We note that HER characteristics are highly reproducible although the multilayer portions slightly vary with different batches of samples (Figures S27–S30 and Table S4, Supporting Information).

Since the catalytically active sites are directly related to EASA, we elucidate the underlying mechanism on active sites in V–MoS$_2$ by performing density functional theory (DFT) calculations. Here, we focus on two main aspects: the Gibbs free energy (\(\Delta G_{\text{H}}\)) with substrates and density of states (DOS) near the Fermi level associated with active sites. Typical chalcogen vacancies on pure MoS$_2$ and V–MoS$_2$ and various substrates including Gr (0002), Cu (111), and Ni (111) are schematically drawn in Figure 3a. The Gibbs free energy at chalcogen vacancy next to Mo sites (Mo-vac$_x$) shows relatively close to the thermoneutral point, although its dependence on the substrate varies slightly (Figure 3b). It is remarkable to reveal the best Gibbs free energy at chalcogen vacancy next to V site (V-vac$_x$) on the Cu substrate is \(-0.02\) eV, nearly ideal 0 eV, while the other substrates (Gr and Ni) are far deviated from the thermoneutral point. The volcano plot is summarized with various materials in the literature (Figure 3c and Figures S31–S33, Supporting Information). While the Gibbs free energy of Mo-vac$_x$ is similar to that of V-vac$_x$ with Cu substrate, the exchange current density of V-vac$_x$ is superior to that of Mo-vac$_x$ (Table S5, Supporting Information). A summary of catalytic parameters of V–MoS$_2$/Cu in comparison with those of Pt and other TMDs catalysts are provided in Table 1.

The charge-transfer to the active site is directly related to the DOS near the Fermi level.\[6,35\] We consider the S vacancies with pristine MoS$_2$, V–MoS$_2$ with two V concentrations, and VS$_2$ on Cu substrate (Figure 3d) and calculate projected DOS (PDOS) of individual atoms in (5 \times 5) unit cell (see Experimental Section). The PDOS of MoS$_2$ with a single S vacancy (Figure 3e) is developed near the Fermi level (\(E_F\)) and is further developed with additional V site in V$_{(9.3\%)}$–MoS$_2$/Cu. The bandgap is closed at this V concentration. In addition to enhanced DOS at V$_{(16\%)}$–MoS$_2$/Cu, the bands are highly degenerate. The bandgap is closed in metallic VS$_2$/Cu and therefore the stability of material is no longer guaranteed. The integrated DOS near the Fermi level is elevated with increasing V concentrations and promotes the electron injection to active sites. The higher the V concentration, the better the exchange current density, but limited by material stability like pure VS$_2$ (Figure 3f).

The nanodispersed VS$_2$ in the semiconducting MoS$_2$ lattice in our study is certainly advantageous in several respects (Figure 3g). The content of chalcogen vacancies in V–MoS$_2$ is...
\[ \Delta G^\circ = 1.0 \times 10^{14} \text{ cm}^{-2} \] at 9.3 at% V concentration, which is about twice the amount of S vacancies in pristine MoS\(_2\). Consequently, the exchange current density meets the industrial target. An additional advantage is that the substrate is highly susceptible to proximate monolayer V–MoS\(_2\), which can be used to engineer Gibbs free energy and electron injection. In particular, the Cu substrate is not only useful to improve the exchange current density but also to tune the Gibbs free energy to the ideal 0 eV, facilitating efficient electron transfer from the Cu substrate to active sites.

Another engineering point is preserving the material stability. In our case, the unstable VS\(_2\) metal is stabilized by introducing nanodispersed VS\(_n\) in the semiconducting MoS\(_2\) lattice. At this stage, raising the V concentration beyond 10% V is limited from a synthesis point of view due to incomplete formation of fully covered V–MoS\(_2\) film (Figure S34, Supporting Information). This is an open question to increase further the V concentration in order to improve catalyst efficiency, while ensuring stability. The exchange current density can be further improved by introducing...
Table 1. The comparison of catalytic parameters of V–MoS$_2$/Cu with Pt and other TMDCs. The comparison of Gibbs free energy for adsorbed hydrogen ($\Delta G_{\text{H}_2}$), overpotential at 10 mV cm$^{-2}$, current density, charge transfer resistance ($R_{\text{ct}}$), and the turnover frequency (TOF) at 0 V of V–MoS$_2$, Pt, and other TMDCs electrocatalysts.

| Catalyst      | $\Delta G_{\text{H}_2}$ [eV] | $\eta_{10}$ [V] | $R_{\text{ct}}$ [k$\Omega$] | TOF @ 0 V [s$^{-1}$] | Reference |
|---------------|--------------------------|----------------|---------------------------|---------------------|-----------|
| Pt            | 0.00                     | -0.04          | 2.2                       | 0.70                | Our work  |
| V–MoS$_2$/Cu  | -0.02                    | -0.08          | 0.80                      | 0.30                | Our work  |
| Nb$_2$WS$_2$  | -0.11                    | -0.15          | 7.40                      | 0.20                | (4)       |
| 1T WS$_2$     | 0.28                     | -0.25          | N/A                       | 0.04                | (11)      |
| V$_2$         | -0.03                    | -0.08          | 27                        | N/A                 | (4)       |
| 1T MoS$_2$    | 0.29                     | -0.22          | 211                       | N/A                 | (14)      |

3D scaffolds such as wrinkles or a porous network. Our strategy provides insight into ways to engineer a single-atom catalyst at the atomic level with 2D materials and furthermore facilitates the design of target-specific characteristics for application to a variety of electrocatalysts, photocatalysts, and electronic devices.

Experimental Section

**Growth of MoS$_2$ and V–MoS$_2$:** V–MoS$_2$ was synthesized using a one-step CVD method. Liquid metal precursors were prepared by mixing two aqueous solutions containing Mo and V precursors, respectively (0.05 m sodium molybdate dihydrate [Na$_2$MoO$_4$·2H$_2$O], Sigma-Aldrich, 331058 and 0.05 m sodium orthovanadate dihydrate [Na$_3$VO$_4$·2H$_2$O], Sigma-Aldrich, S6508). These solutions were mixed in the given ratios to control the concentration of V in MoS$_2$ lattice. The mixed solution was spin-coated onto a SiO$_2$/Si wafer at 2000 revolution-per-minute for 1 min. For the growth of the V–MoS$_2$ film by CVD, the temperature was elevated to 800°C under Ar atmosphere at a flow rate of 50 sccm and then dimethyl sulfoxide as a source of S and H$_2$ at flow rates of 3 and 5 sccm, respectively, were introduced for 10 min. After the growth of the V–MoS$_2$ film, the temperature was naturally cooled under Ar and H$_2$ atmosphere without changing the flow rate. The pristine MoS$_2$ film was synthesized by using the same CVD procedure without adding the V precursor.

**Transmission Electron Microscopy and Specimen Preparation:** Atomic-resolution ADF-STEM images of the samples were acquired using a probe aberration-corrected STEM (JEM-ARM200CF, Jeol Ltd.) operating at 80 keV. The detector angle range for ADF imaging was 45–180 mrad and the convergence semi-angle of the probe was 23 mrad. To avoid electron beam damage, the acquisition time of STEM image was conducted within 10 s (Figure S35, Supporting Information). The multislice method was used for ADF-STEM image simulations, which was implemented in an open software, QSTEM software package[16] and the atomic quantifications from the ADFSTEM images were performed with commercial software qHAADF (HREM Research Ltd.). The TEM sample was prepared by the conventional transfer method with a PMMA C4 (Microchem) supported layer.[18] After transferring the V–MoS$_2$ film onto the TEM grids (PELCO, 200 mesh, copper, 1.2 µm holes), the PMMA layer was removed by acetone. To avoid polymerization residuals during STEM imaging, the V–MoS$_2$ on the TEM grid was annealed at 300°C for 3 h under the forming gas atmosphere prior to TEM analysis.

**Surface Morphology and Chemical State Analysis:** The surface morphology of the as-grown V–MoS$_2$ film was examined by optical microscopy (Nikon LV-IM, Nikon) and SEM (JSM-7100F, JEOL). X-ray photoemission spectroscopy (K-Alpha, THERMO FISHER) was employed to characterize the elemental composition of V-doped MoS$_2$. Confocal Raman and PL measurements were conducted on a Nanobase system (XperRam 100, Nanobase) with an excitation energy of 2.32 eV.

**Electrode Fabrication:** The as-grown V–MoS$_2$ films (1 × 1 cm$^2$) were transferred onto the working electrode (graphite sheet) using a PMMA-supported wet-transfer method.[19] The PMMA was removed in hot acetone for 10 min to obtain a V–MoS$_2$/graphite sheet with a 1 × 1 cm$^2$ active geometric surface area. The procedure was repeated for transfer onto other electrodes (Cu and Ni).

**Electrochemical Measurements:** All electrochemical measurements were conducted on a ZIVE SP2 (ZIVE Lab, Korea) electrochemical workstation within a three-electrode cell in 0.5 M H$_2$SO$_4$ at room temperature. A graphite substrate, saturated calomel electrode (SCE), and graphite rod were used as the working, reference, and counter electrodes, respectively. The electrolyte was de-aerated by purging with N$_2$ for 30 min prior to conducting the electrochemical experiment. Purging was maintained throughout the experiment. The catalytic behavior was characterized using LSV, EIS, cyclic voltammetry (CV), and chronoamperometry measurements. The LSV was measured in the range of 0 to −0.8 V (vs RHE) at a scan rate of 5 mV s$^{-1}$. EIS was measured from 1000 kHz to 10 mHz at an amplitude of 10 mV s$^{-1}$ and a constant potential of −0.3 V. A simple Randles circuit was applied to fit the EIS data using the software Zview. The $C_{\text{dl}}$ was measured by CV between 0.1 and 0.2 V (vs RHE) at scan rates of 5, 10, 20, 30, 40, 50, 60, 80, and 100 mV s$^{-1}$. The stability and durability were studied using chronoamperometry at −0.27, −0.14, and −0.07 V and CV between −0.3 and 0.1 V (vs RHE) at a scanning rate of 100 mV s$^{-1}$, respectively. The potential calibration of the reference electrode (SCE) was performed in high purity hydrogen (purity ≥99.99% H$_2$SO$_4$ solution using Pt foil as working electrode[27] and CV measurement was carried out at 1 mV s$^{-1}$ scan rate. The average of the two potentials which crossed the current at zero was taken as a thermodynamic potential for hydrogen electrode reaction. Therefore, all potentials were converted to RHE using the equation:

$$E_{\text{RHE}} = E_{\text{SCE}} + E_{\text{SCE}}^0$$

where $E_{\text{RHE}}$ was the converted potential value versus RHE, $E_{\text{SCE}}$ was the potential reading from the potentiostat, and $E_{\text{SCE}}^0$ was the experimentally determined standard electrode potential of SCE (0.246 V). A resistance test was conducted prior to measurements, and IR compensation was applied using ZIVE SP2 workstation software. The Ohmic drop was corrected using the current interrupt method, and all potentials were IR-corrected with a compensation level of 90%.

**Turnover-Frequency Calculation:** According to a previous reference,[6] the hydrogen TOF could be calculated using the formula:

$$\text{TOF}(s^{-1}) = \frac{j}{n \times N \times \text{relative EASA} \times (1.602 \times 10^{-19} \text{C})}$$

where $n$, $N$, and relative EASA were the number of electrons required to evolve one mole of hydrogen molecule, the density of active sites, and the EASA of V–MoS$_2$ with respect to the Cu substrate, respectively.

**Relative EASA:**

$$\frac{35.3 \text{ mF cm}^{-2}}{13.8 \text{ mF cm}^{-2}} = 2.73$$

The lattice parameters $a = 3.192$ Å and $c = 13.378$ Å were used for V–MoS$_2$, therefore the surface area of the unit cell was $5.78 \times 10^{-16}$ cm$^2$. Thus, the number of active sites was estimated to be $\approx 1.73 \times 10^{15}$ cm$^{-2}$ presuming that the entire basal plane was catalytically active. Therefore, the geometric density of active sites of V–MoS$_2$ was

$$1.73 \times 10^{15} \text{ cm}^{-2} \times 2.73 = 4.72 \times 10^{15} \text{ cm}^{-2}$$

This was overestimated due to highest active sites at the basal plane. The TOF could be larger in real system. To estimate the TOF at the exchange current density, the TOF was extrapolated linearly from the TOF curve at 0 V.

**Computational Methods:** The spin-polarized DFT calculations were conducted using the Vienna ab initio simulation package.[38] The authors
employed the revised Perdew–Burke–Ernzerhof exchange and correlation functional[39] combined with the introduction of vdW-DF[40] for the non-local correlation part, to accurately account for the dispersion interactions.[41] The projector augmented wave method was used for ion interaction. The Brillouin zone was sampled using a 3 × 3 × 1 k-point mesh, while the electronic states were smeared using the Methfessel–Paxton scheme with a broadening width of 0.1 eV. A 6 × 6 × 1 k-point mesh was used for the DOS calculation. The electronic wave functions were expanded in a plane wave basis with a cutoff energy of 500 eV and the atomic relaxation was continued until the Hellmann–Feynman forces acting on the atoms were less than 0.02 eV Å⁻¹. 2D structures were modeled using a 5 × 5 supercell of MoS₂, and Cu and Ni substrates were modeled by employing slabs consisting of four atomic layers with 2D structures added. A 4 × 8 supercell of MoS₂ on top of a 5 × 10 supercell of the graphene model was used for the MoS₂/graphene structure. In each system, a vacuum layer of 16 Å was added onto the MoS₂ surface to eliminate possible interlayer interactions. The free energy of H adsorption, ΔGₜₜₜ, was defined as ΔGₜₜₜ = ΔEₜₜₜ + ΔEᵥ₂ ∈ − TΔSₜₜₜ, where ΔEₜₜₜ was the H adsorption energy, ΔEᵥ₂ ∈ was the zero-point energy difference, T was room temperature, ΔSₜ was the difference in entropy, and ΔEᵥ₂ ∈ − TΔSₜ was 0.24 eV.[42] ΔEₜₜₜ was defined as ΔEₜₜₜ = E(H⁺ + surface) − E(surface) − 1/2E(H₂), where E(H⁺ + surface), E(surface), and E(H₂) represented the total energies of the H adsorbed surface, pristine surface, and H₂ molecule in the gas phase, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

F.-O.T.-A.-F. and S.J.Y. contributed equally to this work. K.K.K. acknowledges support from the Basic Science Research Program through the National Research Foundation of Korea (NRF), which was funded by the Ministry of Science, ICT & Future Planning (2018R1A2B2002302 and 2020R1A4A3079710), and the Institute for Basic Science (IBS-R011-D1). Y.-M.K. acknowledges financial support by the Hydrogen Energy Innovation Technology Development Program of the National Research Foundation of Korea (NRF) funded by the Korean government (Ministry of Science and ICT (MSIT)) (No. 2019M3J6A1013959). Y.-K.H. acknowledges support from the Basic Science Research Program through the National Research Foundation of Korea (NRF), which was funded by the Ministry of Science, ICT & Future Planning (2019R1A2C1008257). Y.H.L. acknowledges support from the Institute for Basic Science (IBS-R011-D1). S.M.K. acknowledges support from the Basic Science Research Program through the National Research Foundation of Korea (NRF), which was funded by the Ministry of Science, ICT & Future Planning (2020R1A2B5B03002054) and Samsung Research Funding & Incubation Center of Samsung Electronics under Project Number SRFC-MA1901-04.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords

first-principles calculations, hydrogen evolution, molybdenum disulfide, transition metal dichalcogenides, vanadium disulfide

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