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ABSTRACT: Maximizing and creating active sites has been a general strategy to increase the performance of a catalyst. Because of the high electrocatalytic hydrogen evolution reactivity (HER) of ultrafine Mo$_2$C nanocrystals and edges of two-dimensional MoS$_2$, an electrode with a synergistic integration of these two nanomaterials is expected to show a better HER performance. Here we report this hybrid nanostructure of vertically aligned MoS$_2$/Mo$_2$C nanosheets on conductive carbon paper. It was revealed that the original structure of MoS$_2$ nanosheets remains intact after the carburization, but the surfaces are incorporated with either Mo$_2$C nanodomains or a heteroatomic mixture of S and C. The hybrid catalyst exhibits a much lower HER overpotential in comparison to those of the corresponding Mo$_2$C and MoS$_2$ alone. Its high activity is congruent with DFT calculations, which show that multiple S and C coordinated Mo sites with near zero Gibbs free energy of hydrogen adsorption exist. Thus, the low overpotential of this binder-free hybrid catalyst is a result of active sites of Mo$-S-C$ and highly dispersed Mo$_2$C nanodomains on the original edges and basal planes of MoS$_2$. Our prediction and realization of active HER sites with this hybrid two-dimensional nanostructure opens up a route toward the development of more active HER catalysts.

KEYWORDS: vertical MoS$_2$ nanosheets, carburization, Mo$_2$C nanodomains, hybrid nanostructure, hydrogen evolution reaction, Mo$-S-C$ motifs

INTRODUCTION

Considerable attention has been focused on the generation of clean and renewable energy. Hydrogen is a carbon-free clean fuel, and hydrogen production via water electrolysis is considered to be a sustainable and potentially large scale process for the conversion and chemical storage of renewable energy.$^1$ To date, Pt is still the most active hydrogen evolution reaction (HER) catalyst,$^2$ but its high cost and scarcity limits its commercial application. Therefore, it is important to develop low-cost and earth-abundant HER catalysts.$^3$ Mo is more abundant than Pt, and Mo-based compounds have exhibited Pt-like catalytic activity.$^4$ Various nanostructured Mo-based catalysts such as sulfides,$^5-7$ carbides,$^8,9$ nitrides,$^{10}$ and phosphides$^{11}$ have shown high HER performance, but a well-controlled synthesis and assembly of these nanostructures for an efficient HER electrode remains a challenge. For example, two-dimensional MoS$_2$ layers have shown high HER activity,$^5$ but the active sites are only located at the edges.$^{12}$ Methods have hence been developed to either increase the number of active edge sites$^{6,13,14}$ or activate the basal planes$^{15,16}$ but have still met with limited improvement, with overpotentials higher than 100 mV at 10 mA/cm$^2$. Mo$_2$C becomes active only when it becomes ultrafine nanoparticles distributed on carbonaceous supports$^{8,9}$ notwithstanding that synthesis and intimate integration of Mo$_2$C with carbon-based charge-transfer layers are also difficult. Its typical synthesis through reaction between Mo-containing precursors and carbonaceous supports is complicated because of aggregation and sintering of the active sites at high temperature.$^{17-19}$

There are previous reports on MoS$_2$/Mo$_2$C composite materials, but they are not optimized for the HER.$^{20,21}$ In one case, Mo$_2$C nanoparticles were aggregated and MoS$_2$ was not vertically grown on Mo$_2$C nanoparticles$^{20}$ in another case, MoS$_2$ nanosheets and Mo$_2$C nanoparticles were separately attached to carbon nanotubes, and MoS$_2$ nanosheets were not vertically grown on the nanotubes.$^{21}$ In both cases, these powder composites cannot be readily used as HER electrodes. In this work, we combined a hydrothermal method and gas-phase carburization to synthesize free-standing vertical MoS$_2$/

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Mo$_2$C nanosheets for application to the HER. The hybrid nanostructures possess unique structural and catalytic properties derived from MoS$_2$ and Mo$_2$C. Mo$_2$C nanodomains or S–C heteroatoms are directly incorporated into vertical MoS$_2$ nanosheets grown on carbon fiber paper. This binder-free electrode exhibits a low overpotential of 63 mV, much lower than those of corresponding MoS$_2$ and Mo$_2$C. Density functional theory (DFT) calculations further reveal that certain heteroatom structures of Mo–S–C have near zero Gibbs free energy of hydrogen adsorption, a requirement for highly active HER. Our simulation and synthesis method provide a promising strategy to design and fabricate high performance HER electrodes.

**METHODS**

**Synthesis of Vertically Aligned MoS$_2$ Nanosheets.** All chemicals are used as received without further purification. The vertically aligned MoS$_2$ nanosheets were synthesized via a modified method according to refs 22 and 23. Carbon fiber paper was cleaned by diluted HCl (Sigma-Aldrich), deionized water, and acetone (Sigma-Aldrich) with ultrasonication for 5 min in each step. Then the clean carbon fiber was immersed in concentrated H$_2$SO$_4$ (98%, Sigma-Aldrich) for 2 h, followed by washing with DI water and drying at 60 °C overnight. A 335 mg portion of sodium molybdate dehydrate (Sigma-Aldrich) and 112.5 mg of thiourea (Sigma-Aldrich) were dissolved in 20 mL of DI water. The solution was then degassed with N$_2$ gas for 1 h with continuous stirring. Then the solution was transferred to a 50 mL Teflon vessel in a stainless autoclave, and one piece of treated carbon fiber paper (1 cm × 3 cm) was vertically placed into the vessel. The Teflon vessel was then sealed and heated to 200 °C and maintained for 20 h. After the reaction, the autoclave was cooled to room temperature. The product was then washed with copious DI water and ethanol and dried under vacuum at 60 °C overnight. The masses of carbon fiber papers before and after the hydrothermal process were recorded, and the average loading of MoS$_2$ on the carbon fiber paper was 1.67 mg/cm$^2$.

**Synthesis of Vertical Mo$_2$C/MoS$_2$ Hybrid Nanosheets.** In a typical procedure, the as-synthesized MoS$_2$ on carbon fiber paper was placed in a quartz boat which was placed in the center of a quartz tube. The quartz tube was then vacuumed and filled with Ar gas, and this process was repeated twice. Then the quartz tube was heated in a tube furnace at a rate of 5 °C/min in a mixed gas of Ar (400 sccm) and H$_2$ (140 sccm). When the temperature reached 750 °C, CH$_4$ gas (25 sccm) was introduced. The duration time in CH$_4$ gas was varied for 5, 15, 25, and 60 min. After the reaction time, the tube was cooled to room temperature in Ar/H$_2$ gas.

**Characterization.** The morphologies of the as-synthesized samples were first examined by scanning electron microscopy (SEM, FEI XL-30FEG). X-ray powder diffraction (XRD) was carried out on a PANalytical X’pert MPD Pro diffractometer with a Cu target. Transmission electron microscopy (TEM), selected area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDS) were conducted using a JEOL 2010F instrument with an acceleration voltage of 200 kV. For the EDX elemental mapping, samples were carefully scratched off the substrate and dispersed into methanol. The dispersion was then dropped onto a silicon nitride grid. The Raman spectrum was recorded on a Horiba iHR320 spectrometer with an excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI Quantera SXM scanning X-ray microprobe.

**Electrochemical Measurements.** Electrochemical measurements of the as-prepared samples were carried out using a 263A Princeton Applied Research (PAR) potentiostat/galvanostat instrument in a three-electrode configuration with Ag/AgCl and Pt plate (1 cm$^2$) as the reference electrode and counter electrode, respectively. The electrolyte solution was 0.5 M H$_2$SO$_4$ (pH 0.3) which was bubbled with N$_2$ gas for 20 min before use and continuously bubbled during the tests. Linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV/s to obtain the polarization curves. iR correction was automatically made by software equipped with the PAR instrument at 85% compensation. Electrochemical impedance spectroscopy (EIS) was performed at an ac amplitude of 10 mV in a frequency range of 100000 Hz to 10 mHz at preset overpotentials. Before use, samples were cut into a fixed size and then wired using copper wire with silver paste. Epoxy was used to cover the silver paste and the sample with an exposed area of 0.25 cm$^2$. Cyclic voltammetry (CV) was performed at different scan rates in the non-Faradaic reaction potential range to derive the double-layer capacitance for the calculation of electrocatalytically active surface area (ECSA). The potential versus that of the reversible hydrogen electrode (RHE) was calculated with reference to Ag/AgCl according to the Nernst equation $E_{AgCl} = E_{AgCl} = \text{AgCl} + 0.059 \times 0.3 + E_o$, where $E_RHE$ is the potential vs RHE, $E_{AgCl}$ is the measured potential vs Ag/AgCl, and $E_o = 0.2$ V at 25 °C. The long-term stability was evaluated by chronocoulometry measurements at an overpotential of 63 mV. The Faradaic efficiency was obtained by comparing the amount of produced H$_2$ at the electrode with the amount of calculated H$_2$ according to current. The produced H$_2$ was analyzed using a gas chromatograph (GC) equipped with a thermal conduction detector (TCD) with Ar as the carrier gas, which was calibrated with H$_2$ in advance.

**RESULTS AND DISCUSSION**

Vertically aligned MoS$_2$/Mo$_2$C hybrid nanosheets were synthesized via three steps, as shown in Figure 1: (1) clean carbon fiber paper (CFP) was treated with concentrated H$_2$SO$_4$ (98%) for 2 h, followed by washing with deionized water and ethanol and drying at 70 °C for 12 h; (2) the treated CFP was used as the substrate to grow vertically aligned MoS$_2$ nanosheets by a hydrothermal method at 200 °C using Na$_2$MoO$_4$ and thiourea as precursors; (3) Mo$_2$C nano-
sheets were then carburized in Ar/H$_2$/CH$_4$ forming gas at 750 °C. In order to optimize the carburization process, we performed the carburization for 5, 15, 25, and 60 min.

**Figure 2.** SEM images of (a) vertically aligned MoS$_2$ nanosheets and (b) MoS$_2$/Mo$_2$C hybrid nanosheet (the 25 min sample). TEM characterization of the 25 min sample: (c) TEM and (d) HRTEM images. (e) Scanning TEM (STEM) and energy-dispersive X-ray spectroscopy (EDX) elemental mapping images of Mo, S, and C.

**Figure 3.** Composition characterization: (a, b) XPS high-resolution scans of Mo 3d and S 2p of the vertically aligned MoS$_2$ nanosheets and the carburized samples (5, 15, and 25 min); (c) Mo 3d XPS spectra of the 25 min sample; (d) Raman spectra of the vertically aligned MoS$_2$ nanosheets and the 5, 15, 25, and 60 min (Mo$_2$C) samples.

Scanning electron microscopy (SEM) images in Figure S1 in the Supporting Information and Figure 2a show that the CFP substrate becomes covered by dense vertically aligned nano-
sheets with an average thickness of 9 nm. The SEM images in Figure S2 in the Supporting Information show that the surface of the carbon fiber paper after treatment with concentrated H$_2$SO$_4$ became rather rough. We speculate that, during the hydrothermal process, the rough surface may help the adsorption of suboxide MoO$_{3-x}$ species, which were subsequently sulfurized to form homogeneously distributed MoS$_2$ nanocrystals. These nanocrystals serve as seeds for the growth of vertical MoS$_2$ nanosheets. The nanosheet structure remains almost intact after carburization treatment for 5–25 min, but the structure collapses after 60 min of carburization (Figure 2b and Figures S3 and S4 in the Supporting Information). X-ray diffraction (XRD) patterns in Figures S5 and S6 in the Supporting Information indicate that the initial nanosheets are MoS$_2$, but the nanosheets become $\beta$-Mo$_2$C after 60 min of carburization. We refer to the 60 min sample as Mo$_2$C. The other three samples show mixed XRD patterns of MoS$_2$ and Mo$_2$C, suggesting a MoS$_2$/Mo$_2$C hybrid structure.

The transmission electron microscopy (TEM) image confirms the nanosheet morphology. The HRTEM image reveals a disordered crystalline lattice with defects between ordered and disordered nanodomains (Figure S7D in the Supporting Information). This observation is supported by previous reports that MoS$_2$ nanosheets prepared by the hydrothermal method usually have abundant defects on their basal planes. Edge-terminated vertical MoS$_2$ nanosheets provide abundant active edge sites for catalysis. The 25 min sample shows a layered structure with a d spacing measured to be 0.64 nm (Figure 2c), corresponding to the (002) facet of MoS$_2$. The HRTEM image shows clear lattice fringes with interplanar distances of 0.225 and 0.236 nm (Figure 2d), corresponding to the (211) and (020) planes of orthorhombic Mo$_2$C, respectively. X-ray energy dispersive spectroscopy (EDX) elemental mapping images (Figure 2e) suggest that Mo and S are uniformly distributed across the nanosheet. Noticeably, C is localized to isolated nanodomains in comparison to the relatively uniform distribution of Mo and S elements. The TEM characterization of the 60 min sample suggests that MoS$_2$ has been completely converted to Mo$_2$C (Figure S8 in the Supporting Information).

X-ray photoelectron spectroscopy (XPS) analyses were carried out to investigate the chemical composition and valence states. MoS$_2$ shows two characteristic peaks arising from Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ orbitals (Figure 3a), respectively, and a single doublet S 2p peak of the oxidation state of sulfur. Mo 3d$_{5/2}$, Mo 3d$_{3/2}$, and S 2p orbitals of the 5, 15, and 25 min samples shifted to lower binding energy, indicating the successful introduction of C into MoS$_2$, which weakens the
Mo–S bond. The XPS results further demonstrate that after 60 min of carburization MoS2 is completely converted to Mo2C (Figure S9 in the Supporting Information),27,28 since no S 2p signal can be detected. The S 2p spectrum of MoS2 can be fitted with two different doublets (Figure S11 in the Supporting Information): one doublet at 161.9 and 163.1 eV assigned to the S2− or apical S2−, while the carburized samples can only be fitted with one doublet at 161.8 and 162.9 eV corresponding to the S2−. The disulfide-type sulfur (S2−2−) or apical S2− was removed through carburization, indicating the formation of sulfur vacancies on the catalyst surface.31 On the basis of the deconvoluted MoS2 peaks (Figure S10 in the Supporting Information), the content ratios of Mo–C component to Mo–S component are 6.9%, 10.3%, and 13.1% for the 5, 15, and 25 min samples, respectively (Table S1 in the Supporting Information). Increasing the carburization time resulted in an increase in Mo2C content in the hybrid. Raman spectroscopy confirmed that the MoS2 nanosheet structure remains intact after carburization with the two distinct in-plane and out-of-plane modes.32 The relatively higher intensity of the A1g peak in comparison to the E2g1 peak further confirms the edge-terminated structure of the vertical MoS2 and MoS2/Mo2C hybrid nanosheets.26,33

The HER performance of the prepared samples was investigated with a three-electrode setup in 0.5 M H2SO4. Figure 4a,b shows HER polarization curves and corresponding Tafel slopes of the as-prepared samples. The polarization curve of Pt is also shown as a reference.13 The overpotentials to generate a current density of 10 mA/cm2 are 130, 109, 89, and 63 mV for MoS2 and the 5, 15 and 25 min samples, respectively. The corresponding Tafel slopes are 61, 61, 56, and 53 mV/dec, respectively. However, for the 60 min sample (Mo2C), the overpotential increases to 146 mV with a Tafel slope of 63 mV/dec. The 25 min sample has the lowest overpotential and Tafel slope, indicating the best HER performance; it also displays high intrinsic catalytic activity supported by the highest exchange current density. The exchange current density for the vertical MoS2, the 5, 15, and 25 min samples, and Mo2C are 0.05, 0.15, 0.31, 0.9, and 0.051 mA/cm2, respectively. The 25 min sample shows a higher exchange current density in comparison to the reported catalysts in Table S2 in the Supporting Information.

Nyquist plots from electrochemical impedance spectroscopy (EIS) were used to investigate the HER kinetics. As shown in Figure S12 in the Supporting Information, each plot has a similar profile of a semicircle without Warburg impedance in the low-frequency range, suggesting the mass transport is rapid enough so that the reaction is kinetically controlled.34 The charge transfer Tafel slope was determined from the slope of the linear fitting of the plot of log Rct versus overpotential (Figure 4c). These values fall between 39 and 118 mV/dec, indicating that the charge transfer is the rate-determining step.35,36 The 25 min sample still has the lowest charge transfer Tafel slope of 48 mV/dec and the lowest charge transfer resistance of 7.5 Ω (Figure 4d), implying the fastest charge transfer rate.37 The electrocatalytically active surface area (ECSA) was evaluated from the electrochemical double-layer capacitance (Figure S13 in the Supporting Information and Figure 4e).38 The 25 min sample displays the highest value of ECSA, consistent with the best HER performance. The large drop in the Cdl value of the 60 min sample is probably due to the obvious aggregation evidenced by the SEM image. The current densities normalized with the ECSA are shown in Figure S14 in the Supporting Information. We observe that the 25 min sample still shows the highest normalized current density, implying the highest intrinsic catalytic activity. It is also noted that the normalized current density of Mo2C is higher than that of MoS2, indicating the better intrinsic activity of Mo2C in comparison to MoS2. The 25 min sample also has the highest turnover frequency (TOF) of 0.17 s−1 per site at 150 mV overpotential (Figure S15 in the Supporting Information), in agreement with its highest intrinsic activity toward the HER. The TOF of the 25 min sample is comparable to those of the most efficient HER catalysts from previous literature reports, as shown in Table S2 in the Supporting Information.

To optimize the carburization time, we further increased the carburization time to 40 and 50 min. It was found that the overpotential of the 40 and 50 min samples was 94 and 118 mV at a current density of 10 mA/cm2 (Figure S16 in the Supporting Information), respectively, indicating that increasing the carburization time does not further improve the HER performance.
performance. SEM images show that both samples display obvious aggregation (Figure S17 in the Supporting Information). The ECSAs of the 40 and 50 min sample were 86 and 62 m²/cm² (Figure S18 in the Supporting Information), respectively, much lower than that of the 25 min sample. Extending the carburization time induces aggregation and hence results in the decrease of the active site. It is hence concluded that the optimal carburization time is 25 min.

Figure 4f summarizes the overpotentials required for 10 mA/cm² current density and the Tafel slopes of recently developed Mo-S-based and Mo-C-based electrocatalysts, including double-gyroid MoS₂,46 metallic 1-T MoS₂,47 defect-rich MoS₂,48 vertically aligned MoS₂ nanofilms,49 oxygen-incorporated MoS₂,50 strained vacancy MoS₂,51 Mo₂C/CNT,52 edge-terminated MoS₂,53 porous Mo₂C,54 Mo₂C nanosheet/graphene,55 stepped-edge MoS₂,56 and Mo₂C/rGO.57 The performance of the present hybridized sample (the 25 min sample) is better than or at least comparable to that of the most active and recent electrocatalysts.

During HER measurements, Pt dissolution from the counter electrode and redeposition to the working electrode has been demonstrated to have a significant effect on the evaluation of the HER performance of the catalysts.40 We therefore replaced the Pt plate with a graphite rod as the counter electrode to measure the HER performance of the 25 min sample. As shown in Figure S19 in the Supporting Information, it is found that the overpotentials at 10 mA/cm² are very close to each other: 69 mV for the graphite rod counter electrode and 63 mV for the Pt counter electrode. The Tafel slopes are also similar to each other: 60 and 53 mV/dec for graphite rod and Pt, respectively.

The optimized hybrid sample (the 25 min sample) also shows outstanding stability (Figure S20 in the Supporting Information). The cathodic current density shows a slight decay over the duration of 24 h at an overpotential of 63 mV. The polarization curves before and after the long-term operation are almost the same as each other. The hydrogen evolution rate was 0.091 mmol/h, and the Faradaic efficiency was calculated to be 98%. When the electrode after long-term stability test was to be 98%.

Figure 5a shows the polarization curves before and after the long-term operation are almost the same as each other. The hydrogen evolution rate was 0.091 mmol/h, and the Faradaic efficiency was calculated to be 98%. When the electrode after long-term stability test was 0.091 mmol/h, and the Faradaic efficiency was calculated to be 98%. When the electrode after long-term stability test was 0.091 mmol/h, and the Faradaic efficiency was calculated to be 98%. When the electrode after long-term stability test was 0.091 mmol/h, and the Faradaic efficiency was calculated to be 98%. When the electrode after long-term stability test was 0.091 mmol/h, and the Faradaic efficiency was calculated to be 98%. When the electrode after long-term stability test was 0.091 mmol/h, and the Faradaic efficiency was calculated to be 98%. When the electrode after long-term stability test was 0.091 mmol/h, and the Faradaic efficiency was calculated to be 98%. When the electrode after long-term stability test was 0.091 mmol/h, and the Faradaic efficiency was calculated to be 98%. When the electrode after long-term stability test was 0.091 mmol/h, and the Faradaic efficiency was calculated to be 98%. When the electrode after long-term stability test was 0.091 mmol/h, and the Faradaic efficiency was calculated to be 98%.

The Supporting Information illustrates adsorption geometries of H atoms on Mo₂C and the S edge of MoS₂. It is found that the ∆G_ads(n) values for both catalysts cross the neutral value and become positive after all preferential binding sites are filled (Figure S22 in the Supporting Information). The ∆G_ads(n) values for MoS₂ and Mo₂C are not particularly close to zero, but Mo₂C with ∆G_ads(n) = 0.19 eV is somewhat better than the S edge of MoS₂ with ∆G_ads(n) = −0.35 eV.

Modification of MoS₂ by carburization leads to the replacement of S atoms with CH₄ species (x = 0–3) from methane. We therefore introduce the S vacancy and study its formation enthalpy at the S and Mo edge and basal plane, as well as the subsequent CH₄ adsorption enthalpy at that (double) defect site, as summarized in Table S3 in the Supporting Information. We find that the S edge of MoS₂ is most susceptible to carburization and the formation of a mixed Mo–S–C phase, and the selected geometries of the mixed carbo-sulfides forming at the S edge of MoS₂ are illustrated in Figure S5a. It is concluded that ∆E_ads and in turn ∆G_ads exhibit a strong sensitivity to the edge termination and the level of carburization. The calculated differential Gibbs energy as a function of H:Mo ratio for a fully carburized S edge is given in Figure S5b. A unique feature of this plot is the pronounced oscillating behavior of ∆G_ads with increasing H:Mo ratio. Notably, there are three configurations that fulfill the necessary condition of ∆G_ads ≈ 0 eV when 8 (H:Mo = 2), 11 (H:Mo = 2.75), or 12 H (H:Mo = 3) atoms are present at the edge. While the exact structure of the active Mo–S–C sites remains elusive, we note that the high H coverage cases of 11 and 12 H atoms have ∆G_ads ≈ 0 eV, suggesting that certain Mo–S–C motifs are predicted to be suitable HER catalysts with robust performance in the high H coverage limit.

■ CONCLUSION

In summary, we synthesized a unique binder-free electrode comprised of a vertically aligned MoS₂/Mo₂C hybrid nanosheet grown on carbon fiber paper. Systematic characterization indicates that the vertically aligned MoS₂ nanosheets are uniformly hybridized to form Mo₂C nanodomains or heteroatomic mixture of S and C. The hybrid MoS₂/Mo₂C nanosheet electrode shows outstanding HER performance with an overpotential of 63 mV to reach 10 mA/cm² and a low Tafel slope of 48 mV/dec as well as excellent stability. DFT calculations suggest that the high HER performance of the hybrid catalyst is a result of an increased quantity and activity of mixed Mo–S–C sites with near zero Gibbs free energy of hydrogen adsorption formed during the carburization treatment.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b02885.

SEM images and XRD data of the carburized samples, TEM images of MoS₂ and Mo₂C, XPS spectra of MoS₂ and the carburized samples, Nyquist plots and CV curves, normalized polarization curves and TOF, polarization curves using a graphite rod as the counter electrode, electrochemical data and SEM images of the 40 and 50 min samples, electrode stability data and Faradaic efficiency of the 25 min sample, SEM image, Raman spectra, and XPS of the tested 25 min sample, computational methods, and DFT results and discussion (PDF).

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Notes

The authors declare no competing financial interest.

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