Dendritic growth of monolayer ternary \( \text{WS}_2(1-x)\text{Se}_{2x} \) flakes for enhanced hydrogen evolution reaction†

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Two-dimensional transition-metal dichalcogenides (TMDs) have attracted much research interest in the hydrogen evolution reaction (HER) due to their superior electrocatalytic properties. Beyond binary TMDs, ternary TMD alloys, as electrocatalysts, were also gradually acknowledged for their remarkable efficiency in HER. Herein, we successfully synthesized monolayer dendritic ternary \( \text{WS}_2(1-x)\text{Se}_{2x} \) flakes possessing abundant active edge sites on a single crystalline SrTiO\(_3\) (STO(100)). And the obtained dendritic \( \text{WS}_2(1-x)\text{Se}_{2x} \) flakes could be transferred intact to arbitrary substrates, for example, Si\(_x\)O\(_y\)/Si and Au foils. Intriguingly, the transferred dendritic \( \text{WS}_2(1-x)\text{Se}_{2x} \) flakes on Au foil demonstrate a significant HER performance, reflected by a rather lower Tafel slope of ~69 mV dec\(^{-1}\) and a much higher exchange current density of ~50.1 \( \mu \text{A cm}^{-2}\), outshining other CVD-grown two-dimensional TMD flakes. Furthermore, our new material shows excellent stability in electro-catalyzing the HER, suggestive of its robustness for being an excellent electrocatalyst. We believe that this work broadens the outlook for the synthesis of two-dimensional TMDs toward satisfying the applications in electrocatalysis.

Introduction

Recently, two-dimensional (2D) layered transition-metal dichalcogenides (TMDs) have attracted a wide horizon of research interest due to their fascinating optical and electronic properties,\(^1\)-\(^6\) such as a tunable bandgap from indirect to direct when thinned down to a monolayer,\(^7\)-\(^8\) a tunable band structure with strain,\(^9\) highly reactive edge sites for hydrogen evolution reaction (HER),\(^10\) etc. All these properties have made TMDs widely applicable in electronics,\(^11\) optoelectronics,\(^1\),\(^12\) and electrocatalysis.\(^1\),\(^3\)-\(^5\) Hence, for realizing such applications, the synthesis of uniform monolayer TMDs with high crystal quality is an important prerequisite. Compared with numerous growth methods, including mechanical exfoliation,\(^1\) liquid exfoliation,\(^1\) transition metal sulfuration,\(^1\) decomposition of thiomolybdates\(^1\) and physical vapor deposition (PVD),\(^1\) the chemical vapor deposition (CVD) technique has been demonstrated as the most efficient and suitable way to achieve uniform monolayer TMDs due to its tunable parameters and growth substrates.\(^21\)-\(^24\) In fact, CVD-grown TMD triangles on different substrates have been reported meant for electronic and optoelectronic devices exhibiting excellent properties.\(^25\)-\(^27\)

Recently, CVD-grown binary TMD layers, such as MoS\(_2\),\(^28\) MoSe\(_2\),\(^29\) W\(_2\)S\(_3\),\(^30\) and WSe\(_2\),\(^31\) have been synthesized and applied for HER catalysis. It is well known that the edges of TMDs are considered catalytically active due to their low hydrogen binding energy (\(\Delta G_{\text{H}}\)).\(^1\) Furthermore, the electrocatalytic activity for HER linearly correlates with the number of active edge sites of monolayer TMDs.\(^3\) Then much effort has been made to improve the HER activity of TMDs through various techniques such as morphological engineering,\(^3\),\(^2\)-\(^3\) introducing other metal atoms (Co, Ni, Fe)\(^3\),\(^5\) or non-metal atoms\(^3\) into TMD-based electrocatalysts and phase engineering.\(^3\) In this quest, CVD-grown vertical TMD layers,\(^3\) small sized TMD triangles with high nucleation density\(^3\) and dendritic TMD flakes\(^3\) have shown enhanced HER activity owing to their geometrically exposed active edge sites. Moreover, ternary TMD alloys, such as CoS\(_2\)Se\(_2\),\(^3\) nanowires,\(^3\) W\(_2\)(1-x)Se\(_{2x}\) nanotubes,\(^9\) W\(_2\)(1-x)Se\(_{2x}\) nanoribbons\(^4\) and W\(_2\)(1-x)Se\(_{2x}\) particles,\(^4\) synthesized on carbon fibers and Ni foam are also investigated for HER. Consequently, the ternary TMD alloys exhibit a better HER performance than their binary counterparts owing to their many more unsaturated active sites, which is induced by lattice distortion from different radii of atoms on the basal planes. However, compared with 2D binary TMD
layers, the synthesis of ternary monolayer TMD layers for HER is rare and inefficient, especially for monolayer WS$_{2(1-x)}$Se$_{2x}$.

This is perhaps due to its stringent parameter optimization requirements for controlling the S to Se ratio at the monolayer level.

Herein, using a facile low pressure chemical vapor deposition (CVD) method, we initially present a uniform synthesis of monolayer dendritic ternary WS$_{2(1-x)}$Se$_{2x}$ flakes on a single crystalline SrTiO$_3$(STO(100)) substrate. The obtained dendritic WS$_{2(1-x)}$Se$_{2x}$ flakes, decorated with abundant edges on STO (100), can be transferred to arbitrary substrates, for example, SiO$_2$/Si and Au foils without any damage on the material. Notably, the transferred WS$_{2(1-x)}$Se$_{2x}$ flakes on Au foils served as working electrodes in a three-electrode system for catalyzing HER, exhibiting an excellent performance with a low Tafel slope and a rather high exchange current density. Most importantly, it demonstrates impressively excellent stability, suggesting a robust surface of dendritic WS$_{2(1-x)}$Se$_{2x}$ flakes.

**Experimental section**

**Synthesis of dendritic WS$_{2(1-x)}$Se$_{2x}$ flakes and transfer**

In the typical growth, a two-temperature zone chemical vapor deposition (CVD) system was used (ESI†). The dendritic WS$_{2(1-x)}$Se$_{2x}$ flakes were obtained by sulfurization and selenylation of WO$_3$ powder. Sulfur powder was placed in the upstream part of a tube outside the hot zone and mildly sublimated at ∼102 °C by heating belts. And the front zone is loaded with Se powder while the WO$_3$ powder and STO(100) substrates are placed inside the back zone in a proper order. Ar gas (50 standard cubic centimeters per minute (sccm)) and H$_2$ gas (5 sccm) were used to transport WO$_{3-x}$ vapor species to the downstream substrates. The growth pressure was pumped down to about 100 Pa all along the growth process. The growth temperature of WO$_3$ powder and the substrate is ∼860 °C with a heating rate of 30 °C min$^{-1}$, and the temperature of Se powder is 250 °C at a heating rate of 10 °C min$^{-1}$. And the growth time is 30 minutes. The as-grown dendritic WS$_{2(1-x)}$Se$_{2x}$ samples were transferred onto arbitrary substrates with a commonly used method. First, poly(methyl methacrylate) (PMMA) was spin coated on WS$_{2(1-x)}$Se$_{2x}$/STO(100), and then the STO(100) substrates were etched with a concentrated HF solution until detaching the PMMA-capped WS$_{2(1-x)}$Se$_{2x}$/STO(100). Lastly, a clean SiO$_2$/Si substrate or other substrates were then used to “fish out” the PMMA-capped WS$_{2(1-x)}$Se$_{2x}$ film, followed by drying it on a hot-plate (100 °C for 5 min) and removing the PMMA with hot acetone (∼60 °C) for 30 minutes or annealing at 350 °C for 1 h in the furnace.

**Characterization**

The morphologies of dendritic WS$_{2(1-x)}$Se$_{2x}$ and WS$_2$ flakes were characterized by optical microscopy (OM, Olympus BX51 M), Hitachi S-4800 scanning electron microscopy (SEM) and Tecnai F20 transmission electron microscopy (TEM). STEM-EDX elemental mapping was performed by using a Tecnai F20. The optical properties were characterized by using a confocal microscopy-based Raman spectrometer (Renshaw InVia, 532 nm excitation laser). X-ray photoelectron spectroscopy was performed on an ESCALAB 250 Xi. And the thickness of the obtained samples was characterized by atomic force microscopy (AFM, Bruker Icon).

**Results and discussion**

The monolayer dendritic WS$_{2(1-x)}$Se$_{2x}$ flakes with the atom ratio (S:Se) of 19:1 were synthesized on the STO(100) substrate by using a facile low pressure chemical vapor deposition (LPCVD) system (Fig. S1†). The schematic view in Fig. 1a depicts the related chemical reaction of WS$_{2(1-x)}$Se$_{2x}$ flake growth on STO(100). Briefly, WO$_3$ powder was partially reduced by sulfur and selenium vapor to form the volatile suboxide species WO$_{3-x}$, which was further sulfurized and selenized to achieve the formation of WS$_{2(1-x)}$Se$_{2x}$ on the STO(100) substrate. Sulfur powder was placed in the upstream part of the quartz tube and sublimated at ∼102 °C by heating belts, while selenium powder was placed in the front hot zone with a temperature of about 250 °C. And WO$_3$ powder and substrates in the back hot zone were heated to ∼860 °C. Both sulfur and selenium vapor were carried downstream by mixed carrier gas (Ar and H$_2$) and reacted with WO$_3$, finally resulting in the formation of WS$_{2(1-x)}$Se$_{2x}$ on STO(100). It is worth mentioning that the LPCVD system was pumped down to ∼100 Pa in the whole growth process (more details are shown in the Experimental section and ESI Fig. S1†). The photograph in Fig. 1b exhibits a uniform yellow color of the STO(100) after growth, with respect to the left bare STO(100) substrate, which provides physical evidence for the fact that some sort of growth indeed took place. This is more evident from the scanning electron microscopy (SEM) image where the morphology of the as-grown WS$_{2(1-x)}$Se$_{2x}$ on STO(100) is clearly observed in Fig. 1c and S2†. It is apparent that the WS$_{2(1-x)}$Se$_{2x}$ flakes exhibit a relatively uniform thickness and distribution on STO (100). And the gray regions in Fig. S2† are considered as synthesized WS$_{2(1-x)}$Se$_{2x}$ while the dark regions thereabout rep-
The disparate lattice symmetry between WS$_2$(1-x)Se$_2x$ flakes is caused by the presence of Se atoms. Here, the presence of W, S and Se in the nanoflakes can be evidenced. The result of XPS can also provide valuable sources of quantitative information. Accordingly, the atomic ratio of S and Se in WS$_2$(1-x)Se$_2x$ is found to be close to 19 : 1 under an S-saturated atmosphere, which is attributed to the stronger reducibility of S than that of Se. Collectively, the XPS data reveal the formation of ternary WS$_2$(1-x)Se$_2x$ flakes, which is in good agreement with previously reported values.\textsuperscript{40,41} Besides, Raman and photoluminescence (PL) spectroscopic measurements were also performed on the as-grown WS$_2$(1-x)Se$_2x$ on STO(100) (with 532 nm laser excitation). Fig. 1h presents an apparent A excitonic emission located at 625.0 nm, which is in accordance with monolayer ternary WS$_2$(1-x)Se$_2x$. The transfer of the as-grown WS$_2$(1-x)Se$_2x$ from STO(100) to arbitrary substrates is necessary for illustrating their intrinsic properties, as well as for their applications. The schematic view in Fig. 2a clearly displays the fact that our transfer procedure comprises of several steps. Briefly, the transfer method is similar to the commonly used one by detaching the STO(100) substrate with a concentrated HF solution (more details...
are discussed in the Experimental section). Fig. 2b shows the SEM image of an original WS$_2$(1−x)Se$_{2x}$ sample on STO(100) with dendritic design. Using the transfer method mentioned above, the as-grown dendritic WS$_2$(1−x)Se$_{2x}$ flakes on STO(100) can be entirely transferred to the SiO$_2$/Si substrate, as shown in Fig. 2c. Surprisingly, each dendritic WS$_2$(1−x)Se$_{2x}$ flake and its rough edges are still maintained, giving solid evidence of our perfect transfer. And a photograph of the transferred WS$_2$(1−x)Se$_{2x}$ on SiO$_2$/Si, as an inset in Fig. 2c, exhibits a uniform film, again addressing the intact transfer. For the sake of comparison and logical discussion, we synthesized monolayer dendritic WS$_2$ on STO(100) by the LPCVD method and followed the same transfer procedure (details of morphologies are shown in Fig. S5†). Fig. 2d and e depict the Raman and PL spectra, obtained with a 532 nm laser, of monolayer dendritic WS$_2$(1−x)Se$_{2x}$ and WS$_2$ flakes on SiO$_2$/Si. These values are in accordance with those observed for monolayer WS$_2$. It is obvious that there exists a slight red shift in the peaks for monolayer WS$_2$(1−x)Se$_{2x}$ flakes (i.e. 350 cm$^{-1}$ for the E$_{2g}$ mode and 416 cm$^{-1}$ for the A$_{1g}$ mode). From the basis of reported results, the incorporation of other atoms with different radii (Se vs. S) may cause the lattice tensile strain in the formation of WS$_2$(1−x)Se$_{2x}$, and thus induce a red shift of Raman peak positions. What’s more, A$_{1g}$ mode and 2LA(M) mode revealed a stronger intensity compared to that of pure WS$_2$ (normalized by the intensity of the Si peak), which is also attributed to the Se incorporation. Fig. 2e demonstrates the room-temperature PL spectra of pure WS$_2$ and WS$_2$(1−x)Se$_{2x}$ after transferring them from STO(100) to SiO$_2$/Si. Interestingly, the PL peak (~622.6 nm) of WS$_2$(1−x)Se$_{2x}$ exhibits an obvious redshift compared to that of pure WS$_2$ (~618.8 nm). This result suggests that the presence of Se could modulate the bandgap of WS$_2$, along with a red shift of the PL spectrum, in agreement with published results. In this case, the Raman and PL results again confirm the successful introduction of Se atoms and the formation of ternary WS$_2$(1−x)Se$_{2x}$ flakes. Moreover, the obtained dendritic WS$_2$(1−x)Se$_{2x}$ flakes can be transferred intact to arbitrary substrates, building a strong foundation for their broad applications.

In a further step, the WS$_2$(1−x)Se$_{2x}$ flakes were also transferred onto carbon-coated copper grids for transmission electron microscopy (TEM) investigations. The low-magnification TEM image in Fig. 3a shows a continuous film on the copper grids, displaying a successful transfer of our as-grown WS$_2$(1−x)Se$_{2x}$ flakes. And some obvious folding regions could be clearly distinguished around occasionally broken holes according to their different contrasts. The high-resolution transmission electron microscopy (HRTEM) image reveals a perfect hexagonal lattice, as shown in Fig. 3b. And the corresponding selective area electron diffraction (SAED) pattern (200 nm × 200 nm) shown as an inset presents only one set of diffraction spots, highly suggestive of the monolayer nature and the perfect crystal quality of our CVD synthesized WS$_2$(1−x)Se$_{2x}$...
flakes. Moreover, the first-order diffraction spots, corresponding to the (100) planes, demonstrate a d(100) of ~0.27 nm, which is nearly in accordance with that of monolayer WS₂.²⁵ The energy-dispersive X-ray (EDX) spectrum in Fig. 3c demonstrates that the WS₂₁₋ₓSe₂ₓ flakes consist of W, S and Se elements (other element signals come from carbon-coated copper grids), with the S:Se atomic ratio close to 19:1 (x ~ 0.05), indicating the formation of ternary WS₂₁₋ₓSe₂ₓ flakes. This result is in good agreement with the above XPS data. What’s more, the corresponding STEM-EDX elemental mapping of W, S, and Se (Fig. 3d) suggests the uniform distribution of constituents across the WS₂₁₋ₓSe₂ₓ flakes, again confirming their alloy structure. Hence, the TEM images clearly prove the high quality of WS₂₁₋ₓSe₂ₓ flakes and their ternary alloy structure.

To evaluate the electrochemical catalytic performance, the hydrogen evolution reaction (HER) of the synthesized WS₂₁₋ₓSe₂ₓ flakes was investigated using a typical three electrode system in 0.5 M H₂SO₄ electrolyte (N₂ saturated) at room temperature (see the Experimental section). Firstly, monolayer WS₂₁₋ₓSe₂ₓ (or WS₂) flakes were transferred from STO(100) substrates to Au foils, which were used as working electrodes (Fig. S6†). Accordingly, the electrocatalytic performance was measured and linear sweep voltammetric (LSV) measurement was conducted so as to investigate the HER performances of samples under study. For comparison, the HER activities of bare Au foil and transferred dendritic WS₂ on Au foil were also measured and compared with that of dendritic WS₂₁₋ₓSe₂ₓ flakes. As a result, iR corrected polarization curves revealing the respective electrocatalytic performances are depicted in Fig. 4a. It is obvious that the HER performance of Au foil is very poor, suggestive of the fact that the catalytic activity observed for other samples emanates only from the grown materials. At the same current density of 10 mA cm⁻², the dendritic WS₂₁₋ₓSe₂ₓ reveals a much lower overpotential of 156 mV than that of dendritic WS₂ (~310 mV at 10 mA cm⁻²). Hence, the polarization curves demonstrate the promotional effect of Se incorporation in WS₂₁₋ₓSe₂ₓ for HER performance. The Tafel slopes were extracted from the polarization curves in Fig. 4a to evaluate the efficiency of the catalysts, as shown in Fig. 4b. Similarly, the Tafel plot of monolayer dendritic WS₂₁₋ₓSe₂ₓ shows a noticeably lower Tafel slope of 69 mV dec⁻¹ than that of dendritic WS₂ (87 mV dec⁻¹), further solidifying the promotional effect of Se in WS₂. Comparing our findings with other reported and related materials, we found that the Tafel slope of our dendritic WS₂₁₋ₓSe₂ₓ (69 mV dec⁻¹) is much lower than that of reported triangular WS₂₁₋ₓSe₂ₓ flakes (85 mV dec⁻¹).⁴⁶ Similarly, the Tafel slope of dendritic WS₂ is calculated to be 87 mV dec⁻¹, which is also lower than that (100 mV dec⁻¹) of triangular WS₂ flakes.³⁰ These results suggest that the dendritic shape of WS₂₁₋ₓSe₂ₓ (and WS₂) flakes provides many more active edge sites than triangular flakes, thereby resulting in an improved HER performance. Therefore, the dendritic edges as well as Se incorporation of WS₂₁₋ₓSe₂ₓ flakes also play a significant role in the enhanced HER performance. By extrapolating the Tafel plot, the exchange current densities (Fig. 4c) for dendritic WS₂₁₋ₓSe₂ₓ and WS₂ are found to be 50.1 μA cm⁻² and 3.16 μA cm⁻², respectively. The higher exchange current density of WS₂₁₋ₓSe₂ₓ should be attributed to the Se-induced catalytic activity in the basal plane, which is confirmed by the increased Cdl value of dendritic WS₂₁₋ₓSe₂ₓ flakes in Fig. S7.† Additionally, electrochemical impedance spectroscopy (EIS) at 0.15 V versus RHE is employed to investigate the charge-transfer mechanism of HER. The Nyquist plots, in Fig. 4d, reveal that the charge-transfer resistances (Rct) of WS₂₁₋ₓSe₂ₓ and WS₂ flakes are 225 Ω and 860 Ω, respectively. Besides, the series resistance (Rs) observed for WS₂₁₋ₓSe₂ₓ shows a rather low value of 1.8 Ω (inset plot of Fig. 4d), suggesting the small Ohmic loss between the electrolyte and the surface of the electrode. Notably, the smaller Rct and Rs of dendritic WS₂₁₋ₓSe₂ₓ compared to that of pure WS₂ reflect the Se incorporation in WS₂₁₋ₓSe₂ₓ promoting a more efficient charge transfer on the surface of WS₂₁₋ₓSe₂ₓ. Collectively, the HER tests reveal excellent electrocatalytic properties of our obtained dendritic ternary WS₂₁₋ₓSe₂ₓ flakes.

It’s well known that the durability of a catalyst is another important aspect to evaluate its capability for realizing the long term usage. To this aim, the stability of a monolayer dendritic WS₂₁₋ₓSe₂ₓ electrocatalyst was tested via an accelerated disintegration test and the result is shown in Fig. 5a. After 1000 cycles of cyclic voltammetry (CV) run, there results a negligible decay in the performance of dendritic WS₂₁₋ₓSe₂ₓ ele-
trocatalysts, indicative of their excellent stability in the HER. Given the advantageous features obtained from its monolayer nature, dendritic designed flake appearance and Se incorporation, the ternary WS$_{2(1-x)}$Se$_{2x}$ is a better electrocatalyst in HER compared with WS$_2$. As a proof of concept and based on previously reported theoretical and experimental results, the HER activity of binary TMD flakes mainly relates to the edge density and the basal surface is thought to be catalytically inert. But, recently reported studies proposed that the basal plane of ternary alloys (for example, WS$_{2(1-x)}$Se$_{2x}$) is also catalytically active. This is due to the fact that the different atomic radii of Se and S atoms may induce the crystal distortion and lattice strain on the basal plane, leading to the advent of sites convenient for catalytic activity on the basal plane. Hence, a tentative schematic model in Fig. 5b provides an inference that the improved HER performance of dendritic WS$_{2(1-x)}$Se$_{2x}$ flakes is attributed to not only the abundant edge sites but also the active basal plane. Note that the schematic view in Fig. 5b provides only a tentative illustration, but it also gives important guidance.

**Conclusions**

In summary, we have achieved monolayer dendritic ternary WS$_{2(1-x)}$Se$_{2x}$ flakes on single crystalline STO(100) with a facile LPCVD method. The obtained dendritic WS$_{2(1-x)}$Se$_{2x}$ flakes decorated with abundant edge sites can be transferred intact to arbitrary substrates, such as SiO$_2$/Si and Au foils. Intriguingly, our synthesized monolayer dendritic WS$_{2(1-x)}$Se$_{2x}$ flakes on Au foil exhibit a much higher electrocatalytic activity than dendritic WS$_2$ flakes and the reported triangular WS$_{2(1-x)}$Se$_{2x}$ flakes in acid media. Notably, the dendritic shape and Se incorporation of WS$_{2(1-x)}$Se$_{2x}$ flakes play a significant role for the improved HER activity. The transferred WS$_{2(1-x)}$Se$_{2x}$ flakes on Au foil exhibit a low overpotential of ~156 mV at 10 mA cm$^{-2}$, a rather low Tafel slope of ~69 mV dec$^{-1}$ and a higher exchange current density of ~50.1 mA cm$^{-2}$. Moreover, excellent durability suggests that the dendritic WS$_{2(1-x)}$Se$_{2x}$ flake is a perfect candidate for highly efficient electrocatalysis in HER.

This work will pave a new way for fabricating electrocatalysts and other electronic devices.

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (No. 61625401, 61574050 and 11674072), the Ministry of Science and Technology of China (No. 2016YFA0200700), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDA09040201), and the CAS Key Laboratory of Nanosystem and Hierarchical Fabrication. The authors also gratefully acknowledge the support of Youth Innovation Promotion Association CAS.

**Notes and references**
