Supporting Information

Synthesis of crystalline WS$_3$ with layered structure and desert-rose-like morphology

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Discussion on determining the composition of WS$_3$ sample

Inductively-coupled-plasma-based quantitative analysis methods, for example, inductively coupled plasma optical emission spectrometry (ICP-OES), are very useful tools for analysis of compositon because of their good accuracy. However, Proper digestion method is crucial for accurate analysis of solid samples. The main issue for our WS$_3$ sample is the digestion of S anions. Because of the volatile species of S, such as H$_2$S and SO$_x$, digestion based on closed vessels is necessary. Teflon vessel is not recommended for digestion of S because it may cause loss of S analyte.[1] Therefore, specially designed high-pressure quartz vessels were employed in some papers for accurate digestion of S, either using high pressure asher[2] or microwave digestion system.[3]

Unfortunately, we did not have access to the high-pressure quartz vessel. So, we tried autoclave with Teflon vessel for digestion of our WS$_3$ sample. We took two fractions from the very same WS$_3$ sample for digestion and measured the concentration of W and S with ICP-OES. The S/W ratios were 2.44 ± 0.04 for one fraction and 2.06 ± 0.08 for another. The large inconsistency indicates a significant loss of S during the digestion and thus an underestimation of the S/W ratio. Therefore, the results of our ICP-OES measurements were not able to reflect the real composition of the WS$_3$ sample and were not included in the manuscript.

In order to determine the composition of WS$_3$ as best we can, we carried out not only the

XPS analysis but also the thermogravimetric experiments, as discussed in the manuscript.
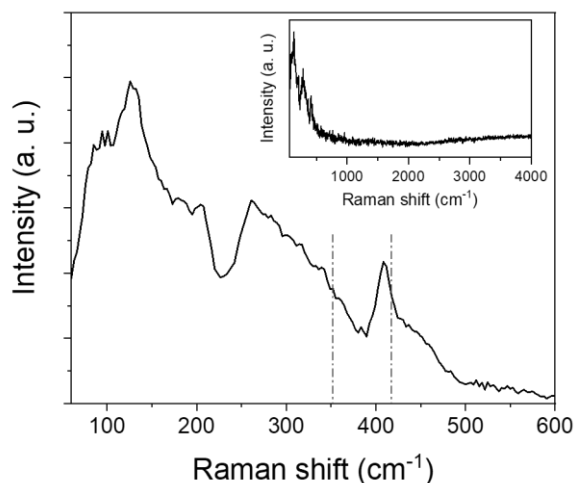
Figure S1. Raman spectra of the WS_3 sample (excitation laser wavelength: 532 nm). The two dashed line mark the positions of the two typical peaks of WS_2. The full spectrum from 50 to 4000 cm^{-1} is shown in the inlet, where no peak is found beyond 600 cm^{-1}. The Raman bands of the WS_3 are totally different from the WS_2.
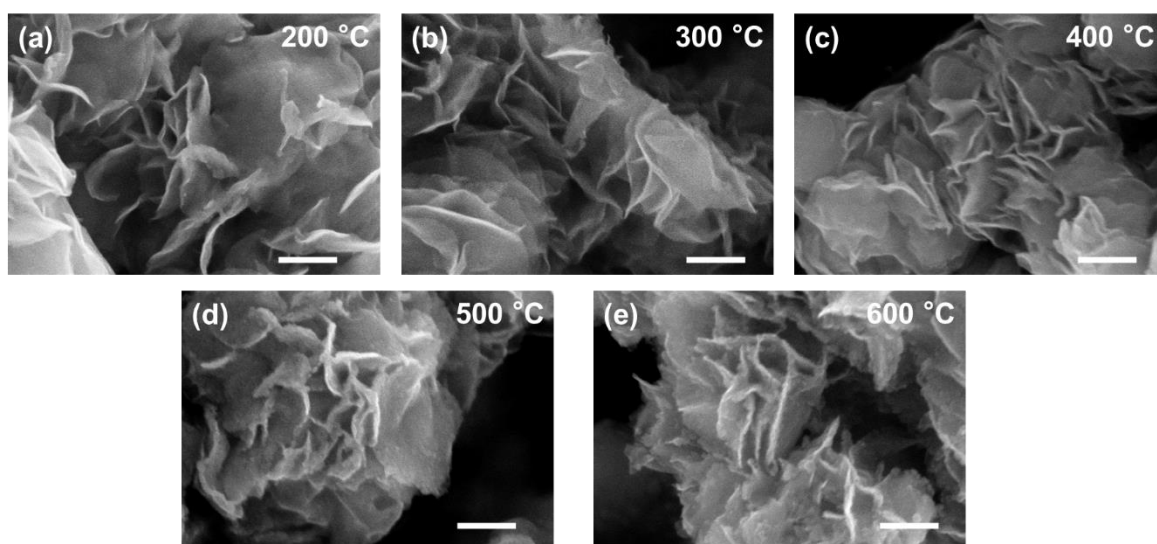
Figure S2. Scanning electron microscopy images of annealed WS_3 at different. The annealing temperatures are 200 °C (a), 300 °C (b), 400 °C (c), 500 °C (d), and 600 °C (e), respectively. The scale bar is 200 nm.

Table S1. Activities of tungsten sulphides as electrochemical catalyst for HER.

	Preparation method	Overpotential (mV)	Tafel slope (mV/dec)	Ref.
WS$_3$	Sulphurization of WO$_3$·0.33H$_2$O with thioacetamide in DMF	130	86	This work
WS$_{2.64}$	Electrodeposition from (NH$_4$)$_2$WS$_4$ solution	~ 390	43.7	[4]
WS$_2$	Sulphurization of WCl$_6$ with S in oleylamine	~100	48	[5]
WS$_2$	Reaction of WO3 with S at 830 ° C on Au foil	110	100	[6]
WS$_2$	CVD reaction of W foil and S	~100	54	[7]
WS$_2$ (both 1T and 2H)	Lithium intercalation and exfoliation from bulk WS$_2$	80–100 (1T) 150–200 (2H)	~60 (1T) ~115 (2H)	[8]
WS$_2$ (1T)	Microwave-assisted intercalation and exfoliation from CVD-grown WS2	~75	70	[9]
WS$_2$ (1T)	Surfactant-Assisted Exfoliation from bulk WS$_2$	90	51	[10]
WS$_2$ (mainly 1T')	Sulphurization of (NH$_4$)$_2$WO$_4$ with thiourea in oleylamine	~120	50.4	[11]
WS$_2$/rGO	Hydrothermal reaction of WCl$_6$, thioacetamide, and graphene oxide	150-200	58	[12]

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