Supporting Information for

Open-ended $W_{18}O_{49}$-filled Tungsten Dichalcogenides Nanotubes Grown on W Substrate to Efficiently Catalyze Hydrogen Evolution

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Supplementary Figures

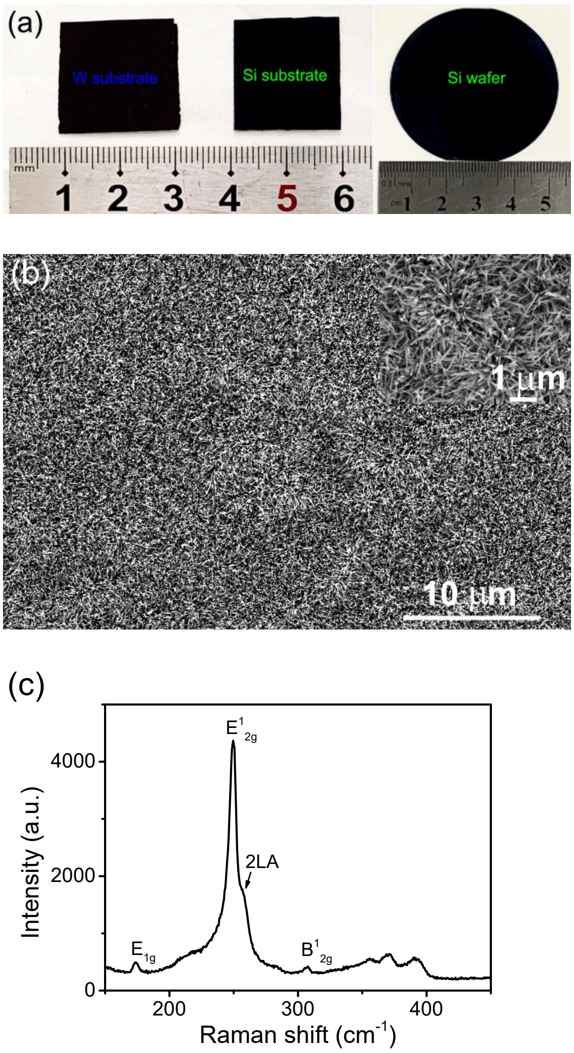


Fig. S1 (a) Photos of WSe_2-based one-dimensional nanostructure films grown on 2 cm-sized W substrate (left)/Si substrate (mid), or 2-inch Si wafer (right), **(b)** SEM image of WSe_2-based one-dimensional nanostructure films grown on a W substrate, **(c)** Raman spectrum of WSe_2-based one-dimensional nanostructured film.

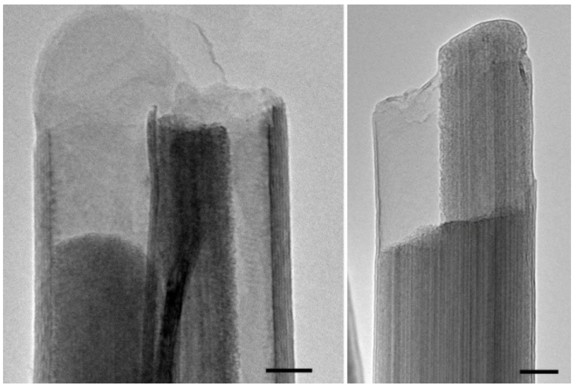


Fig. S2 HRTEM images of WSe_2 uncapped nanotubes (scale bars: 10 nm)

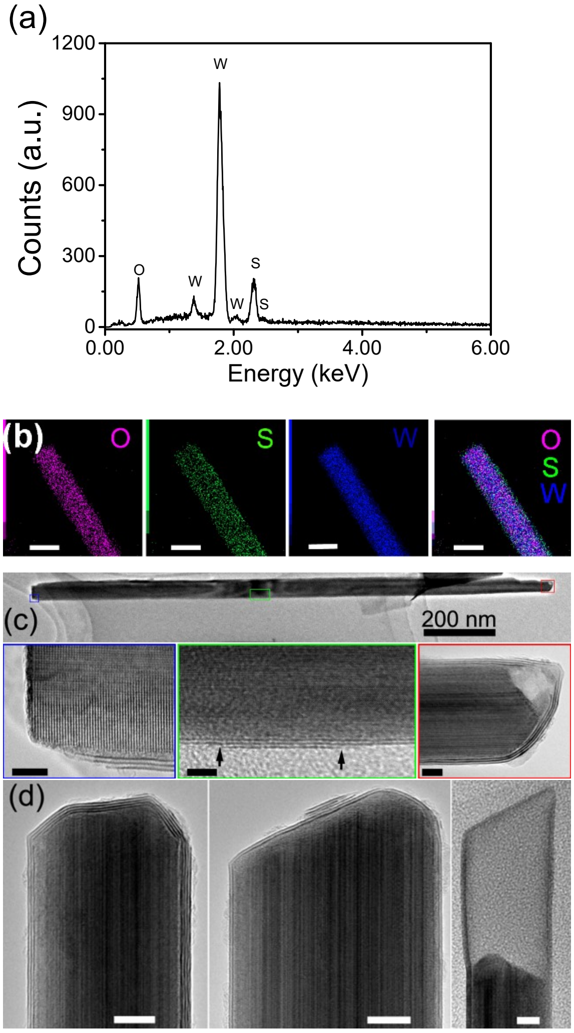


Fig. S3 (a) EDX spectrum of WS_2 -based nanostructure film, **(b)** EDS elemental mappings of a WOx-filled WS_2 nanotube (scale bars: 100 nm), **(c)** TEM image of a WOx-filled WS_2 nanotube capped at top-end and its corresponding HRTEM images taken on 3 different sections highlighted in blue/green/red frames (scale bars: 5 nm), **(d)** HRTEM images of WOx-filled WS_2 capped nanotubes (scale bars: 10 nm).

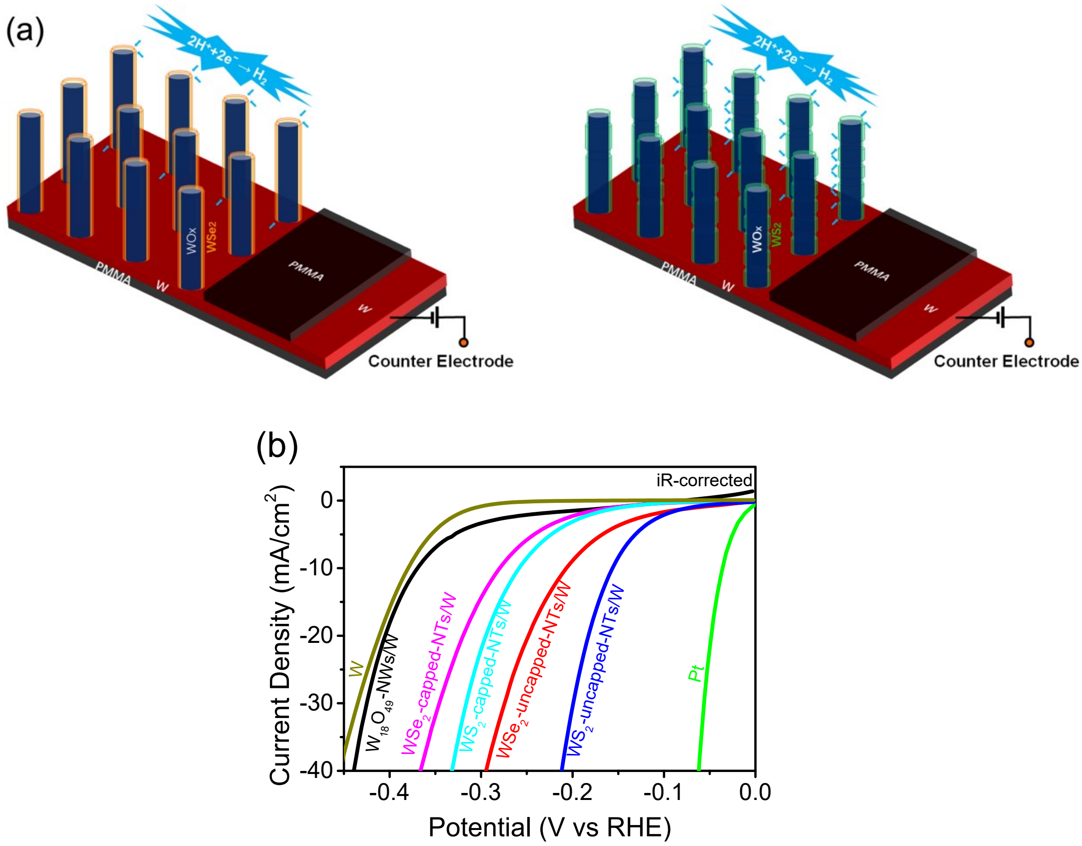
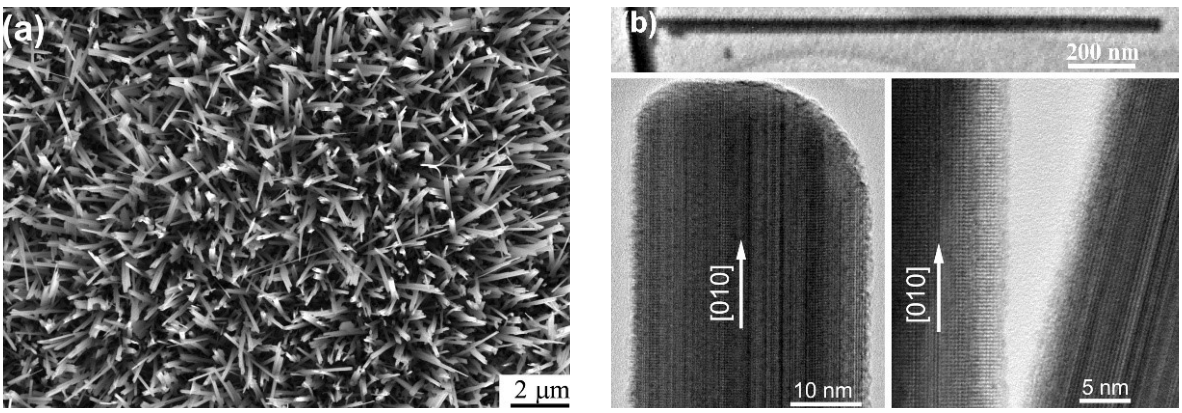


Fig. S4 (a) Schematic drawings of aligned WSe_2 uncapped nanotube working electrode (Left) and aligned WS_2 uncapped nanotube working electrode (Right), **(b)** LSV curves at low-currents for different working electrodes.



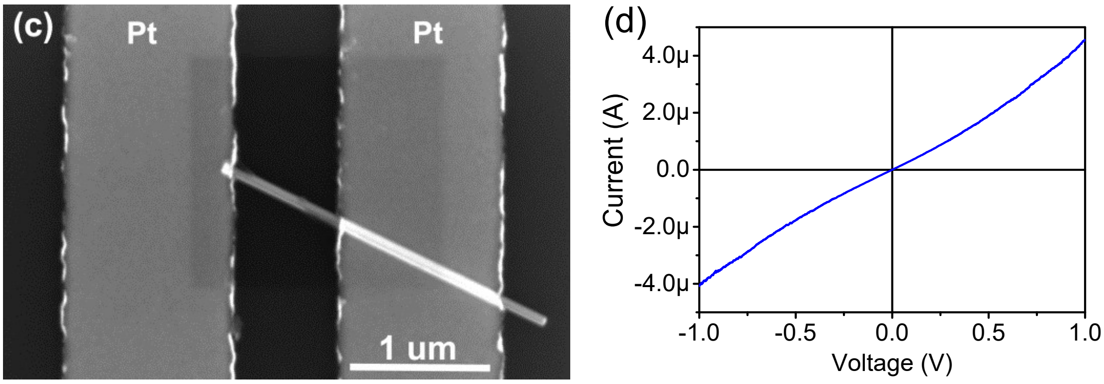


Fig. S5 **(a)** SEM image of aligned $W_{18}O_{49}$ nanowires grown on W substrate, **(b)** TEM images of $W_{18}O_{49}$ nanowires, **(c)** and **(d)** SEM image and corresponding I-V plot of a two-terminal $W_{18}O_{49}$ nanowire device.

Table S1. Comparison between various TMDs-derived nanocatalysts for HER in 0.5M HSO_4 electrolytes

TMDs nanostructured catalyst	**Type**	**η10 (mV)**	**Tafel slope (mV/dec)**	**J_0 @ 0 V (mA/cm^2)**	**Refs**
uncapped WS_2 nanotube arrays/W substrate	thin film	156	85	0.20	This work
nanoporous MoS_2/FTO substrate	thin film	230	50	NA	12
nanoporous MoS_2 /Mo substrate	thin film	280	50	NA	13
WS_2/WO_3 nanohelixes arrays/W substrate	thin film	168	NA	NA	14
MoS_2-MoO_3 nanocables/FTO substrate	thin film	240	50-60	NA	16
WSSe nanotubes/carbon fiber	thin film	~270	105	0.029	20
WS_2 nanosheets/glassy-carbon	powder	NA	55	0.02	8
WS_2 nanosheets/rGO	powder	~270	58	NA	9
single-layer MoSSe nanodots	powder	140	40	NA	10
WS_2 nanosheets/mesoporous graphene	powder	117-142	56-60	NA	11
WS_2 nanoribbons	powder	225	68	0.01	26

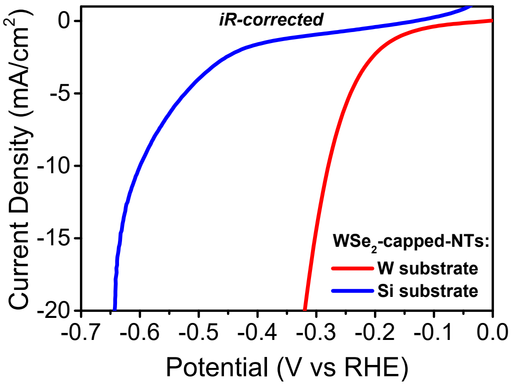


Fig. S6 LSV curves of WSe_2-capped-nanotubes thin film catalyst grown on Si/W substrates

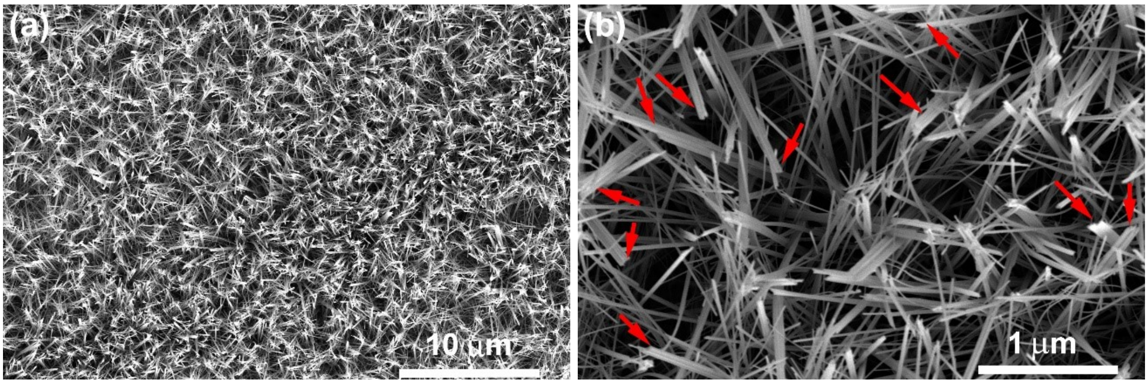
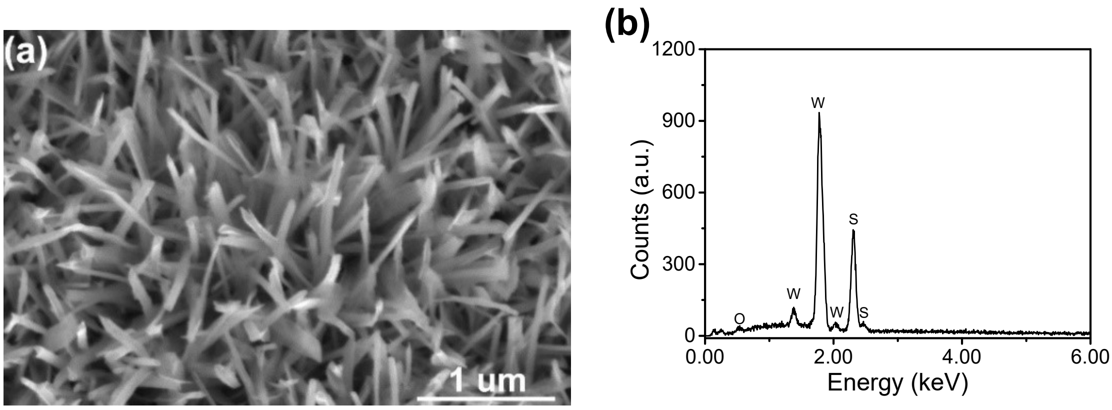


Fig. S7 SEM images of W-supported WS_2 uncapped nanotubes after electrochemical stability testing



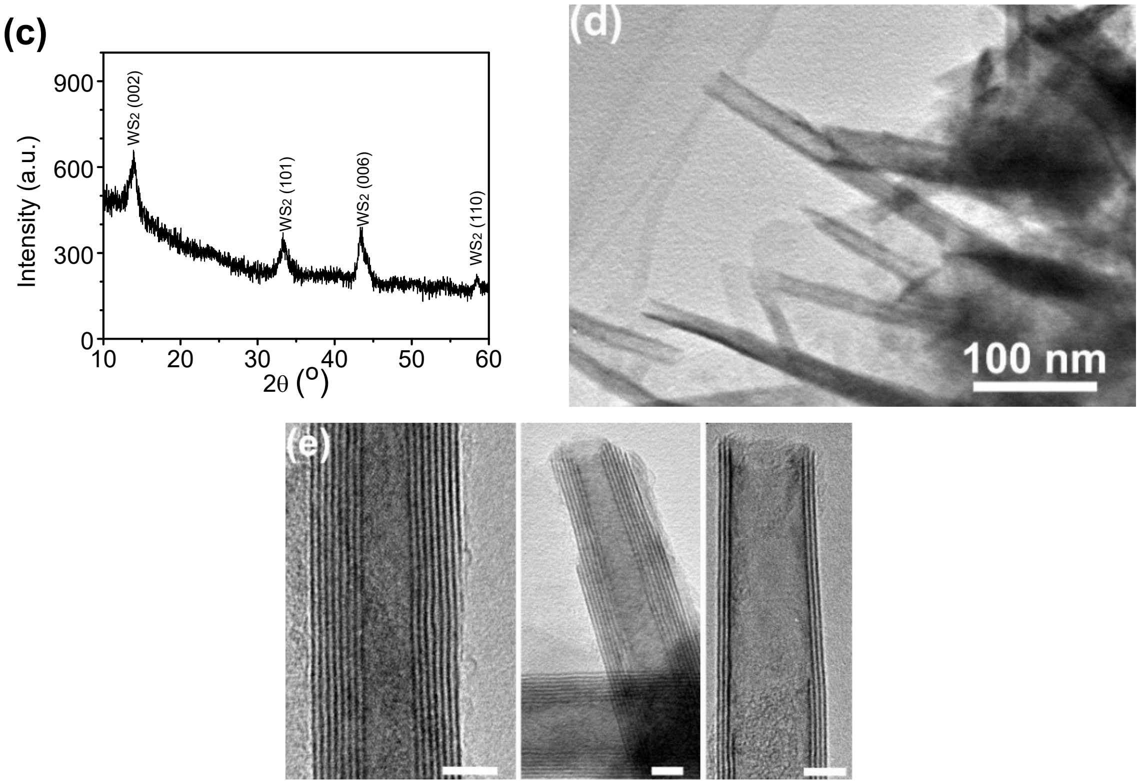


Fig. S8 (a) SEM image of the film after wet etching in diluted HF etchant, **(b)** EDS spectrum of remaining one-dimensional nanostructures, **(c)** GI-XRD spectrum of one-dimensional nanostructures, **(d)** TEM image of WS_2 nanotubes, **(e)** HRTEM images of WS_2 nanotubes (scale bars: 5 nm)

To get pure WS_2 nanotubes by removing tungsten sub-oxide cores, as-grown WOx-filled WS_2 nanotube film was etched in 3% HF aqueous solution for 24 hours, and subsequently rinsed in deionized water for several times before final blow dry with N_2 gas. One-dimensional nanostructures still remained in approximately vertical alignment after etch (Fig. S8a). As shown in Fig. S8b, very little trace of O element was detected by EDS. XRD spectrum shown in Fig. S8c demonstrated that the film was composed of pure 2H-WS_2 phase, indicating the sub-oxide cores were completely removed. Further TEM characterizations verified the formation of pure WS_2 nanotubes, as seen from the low-magnification TEM image in Fig. S8d. HRTEM images of some individual WS_2 nanotubes are displayed in Fig. S8e, showing their characteristics of broken outmost layer or open-ends.