Supplementary Material

Surface Modification towards Integral Bulk Catalysts of Transition Metal Borides for Hydrogen Evolution Reaction

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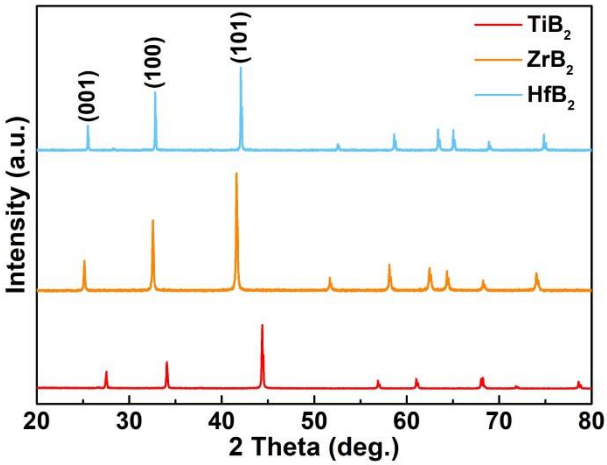

Figure S1. The XRD of commercial TiB_2, ZrB_2, and HfB_2.

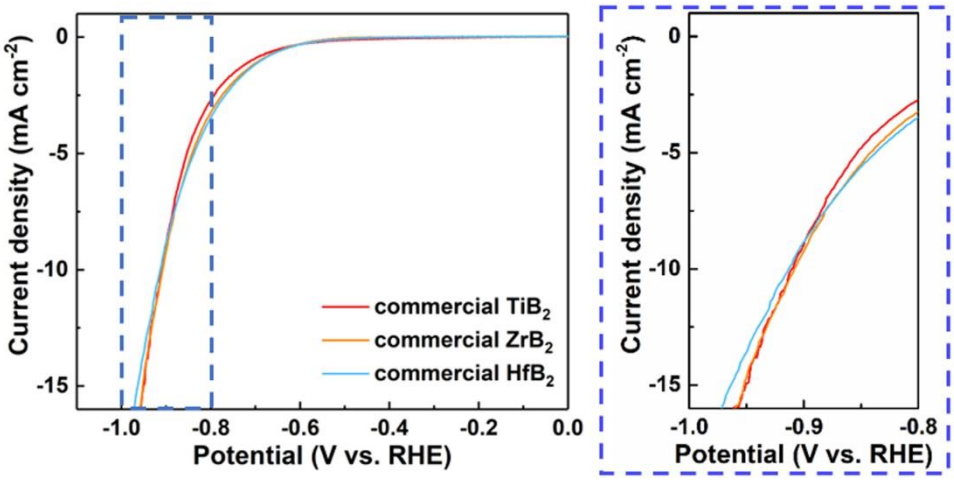

Figure S2. The linear sweep voltammetry (LSV) curves of commercial TiB_2, ZrB_2, and HfB_2 for HER in 0.5 M H_2SO_4 solution.

Table S1. Comparison of the catalytic activity of TiB_2, ZrB_2, HfB_2 obtained herein with those reported previously. (The Current density is 10 mA cm^{-2}.)

Catalyst	Catalysis condition	Overpotential at the corresponding j	Reference
TiB_2 after HCl etching	**0.5 M H_2SO_4**	**346 mV**	**This work**
TiB_2@PPy	0.5 M H_2SO_4	432 mV	[1]
TiB_2 after HPHT	0.5 M H_2SO_4	477 mV	This work
TiB_2 powder	0.5 M H_2SO_4	~490 mV	[2]
Commercial TiB_2 powder (~500 nm)	0.5 M H_2SO_4	848 mV	[1]
Commercial TiB_2	0.5 M H_2SO_4	910 mV	This work
Commercial TiB_2	0.5 M H_2SO_4	~1070 mV	[3]
TiB_2 powder	0.5 M H_2SO_4	~1100 mV	[4]
ZrB_2 after HCl etching	**0.5 M H_2SO_4**	**542 mV**	**This work**
ZrB_2 powder	0.5 M H_2SO_4	~580 mV	[2]
ZrB_2 after HPHT	0.5 M H_2SO_4	627 mV	This work
Commercial ZrB_2	1 M H_2SO_4	690 mV	[5]
ZrB_2 powder	0.5 M H_2SO_4	700 mV	[6]
Commercial ZrB_2	0.5 M H_2SO_4	908 mV	This work
Commercial ZrB_2	0.5 M H_2SO_4	~970 mV	[3]
HfB_2 after HCl etching	**0.5 M H_2SO_4**	**515 mV**	**This work**
HfB_2 after HPHT	0.5 M H_2SO_4	563 mV	This work
HfB_2 powder	0.5 M H_2SO_4	~850 mV	[2]
Commercial HfB_2	0.5 M H_2SO_4	913 mV	This work
Commercial HfB_2	1 M H_2SO_4	>1000 mV	[5]
Commercial HfB_2	0.5 M H_2SO_4	~1050 mV	[3]