Electronic Supplementary Information

3D Nanoporous Ni/V_2O_3 Hybrid Nanoplate Assemblies for Highly Efficient Electrochemical Hydrogen Evolution

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This file includes Fig. S1-S15 and Table S1-S3.

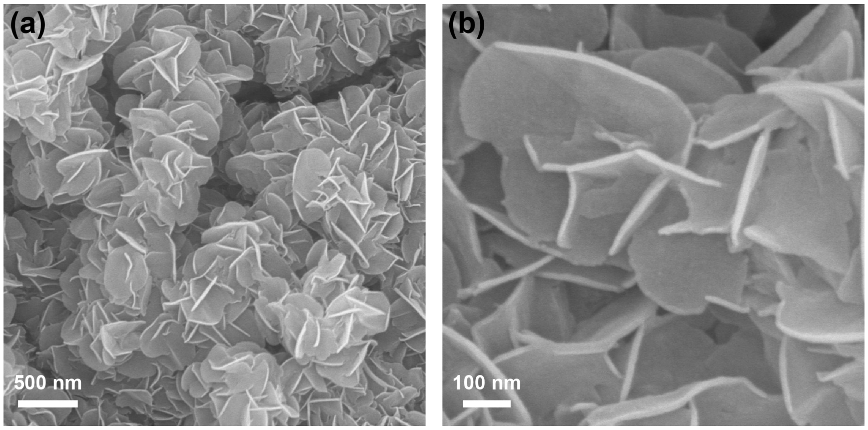

Fig. S1. (a-b) SEM images of Ni-V-O precursor.

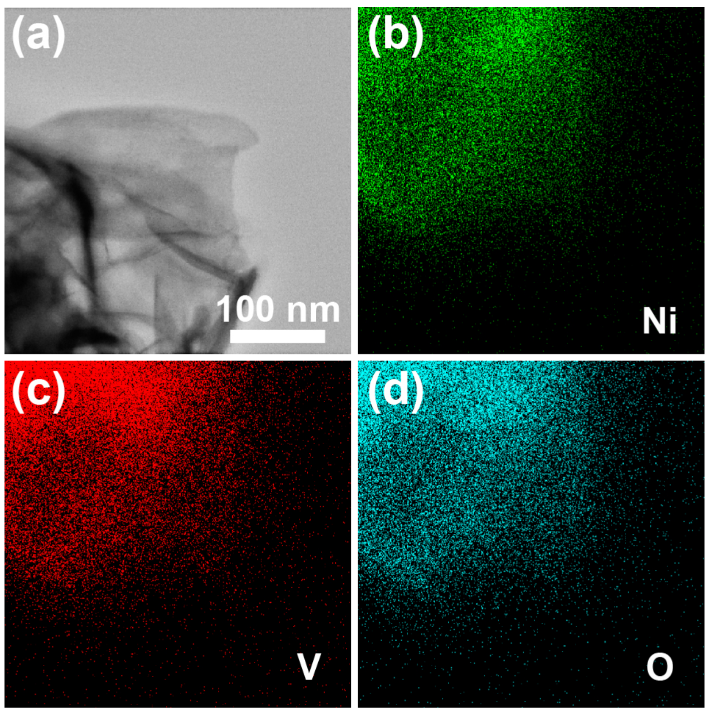

Fig. S2. (a) STEM image and EDS elemental mapping images of (b) Ni, (c) V, and (d) O for Ni-V-O precursor.

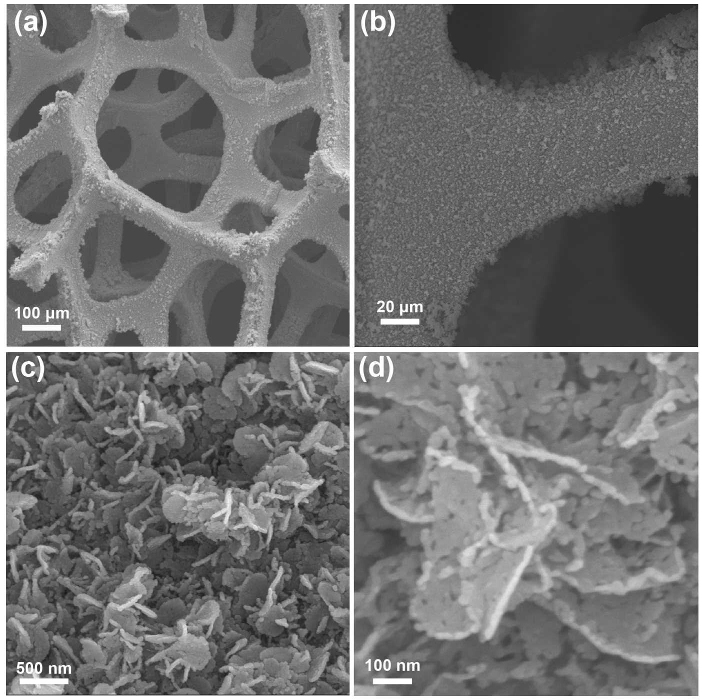

Fig. S3. (a-d) SEM images of Ni/V_2O_3 (Ni/V_2O_3-400).

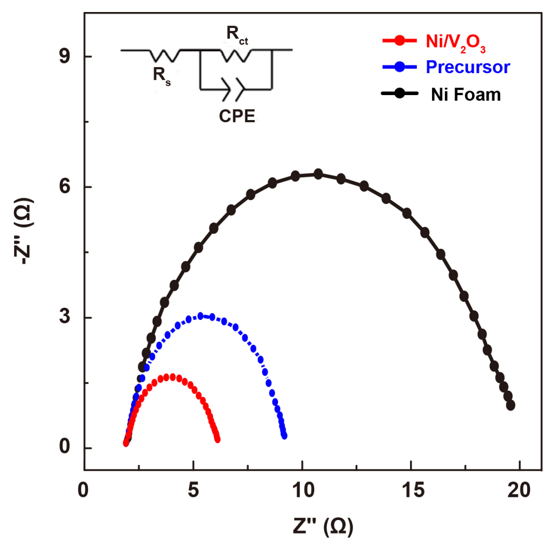

Fig. S4. EIS Nyquist plots at the overpotential of 300 mV for Ni/V_2O_3, precursor and Ni foam.

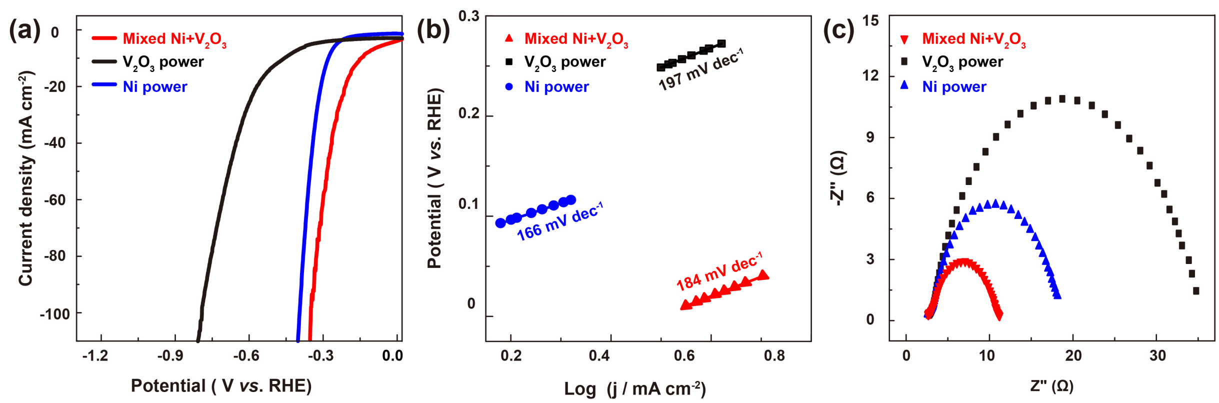

Fig. S5. (a) Polarization curves, (b) corresponding Tafel plots. (c) EIS Nyquist plots at the overpotential of 350 mV for commercial Ni powder, V_2O_3 powder, and its mixture.

Although the commercial Ni/V_2O_3 composite exhibits a lower Tafel slope than commercial Ni powder, it still shows the smallest onset potential (-0.08 V) among three catalysts. This suggests that the intrinsic activity of commercial Ni/V_2O_3 composite is higher than both commercial Ni and V_2O_3 since the onset potential is directly dependent on the intrinsic activity of active sites. Additionally, the R_{ct} of commercial Ni/V_2O_3 composite is smaller than both commercial Ni and V_2O_3, agreeing with its best intrinsic electrocatalytic activity for HER. Basis on these results, it is reasonable to believe that there are synergistic effects between Ni and V_2O_3 for HER.

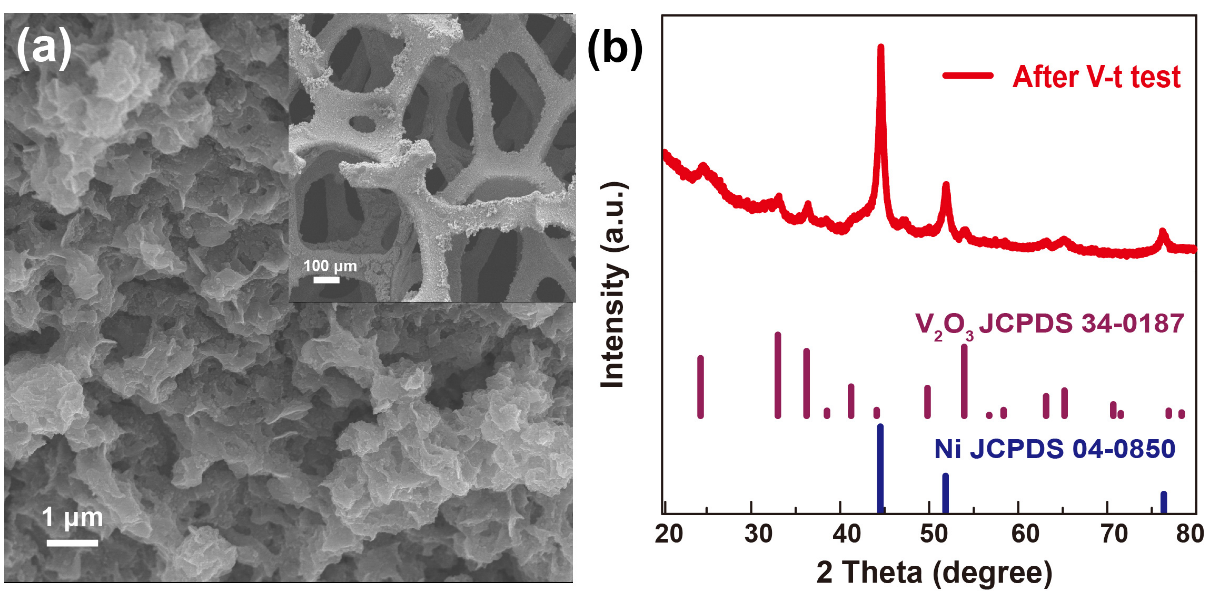

Fig. S6. (a) SEM image and (b) XRD pattern of Ni/V_2O_3 after stability test.

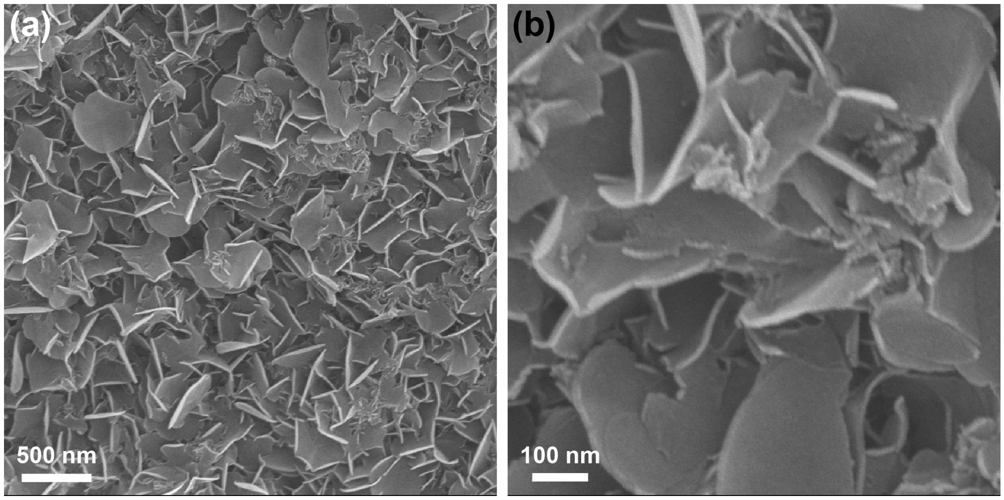

Fig. S7. (a-b) SEM images of Ni/V_2O_3-300.

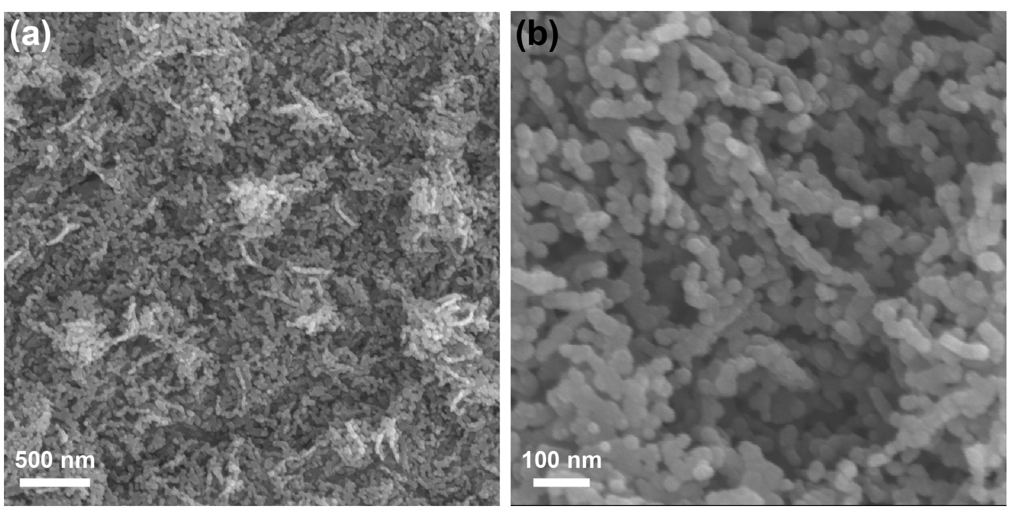

Fig. S8. (a-b) SEM images of Ni/V_2O_3-500.

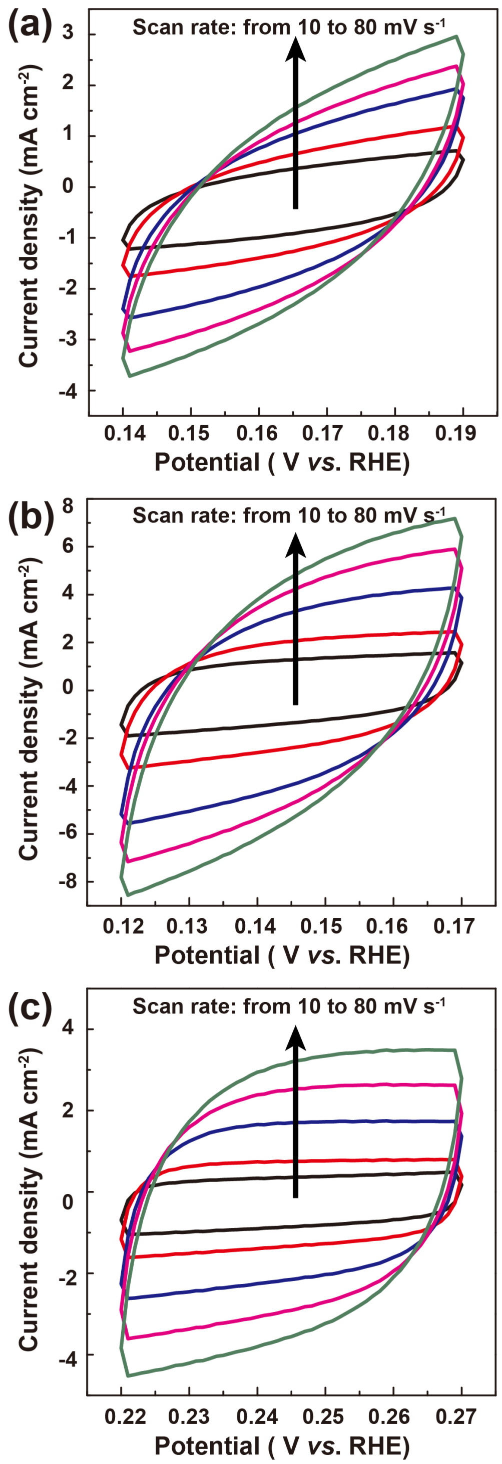

Fig. S9. CV curves measured at different scan rates from 10 to 80 mV s^{-1} in 1 M KOH for Ni/V_2O_3 samples annealed at different temperatures: (a) Ni/V_2O_3-300, (b) Ni/V_2O_3-400, and (c) Ni/V_2O_3-500.

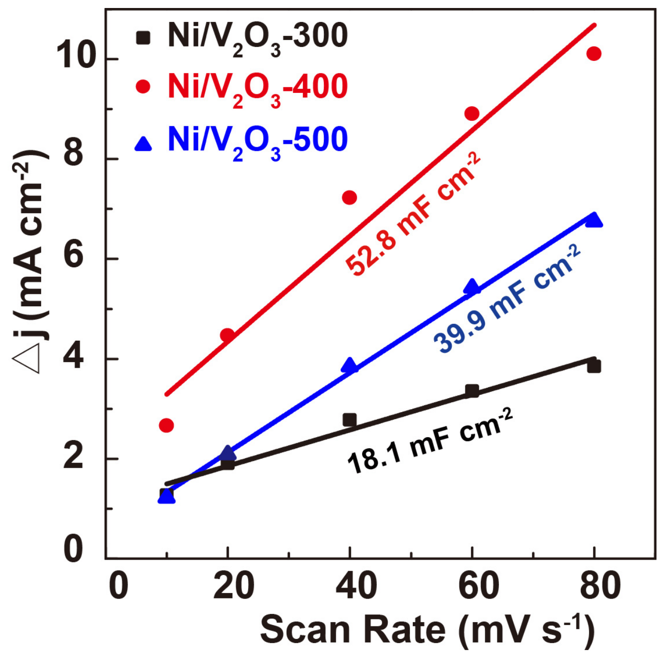

Fig. S10. The capacitive current plots as a function of scan rates.

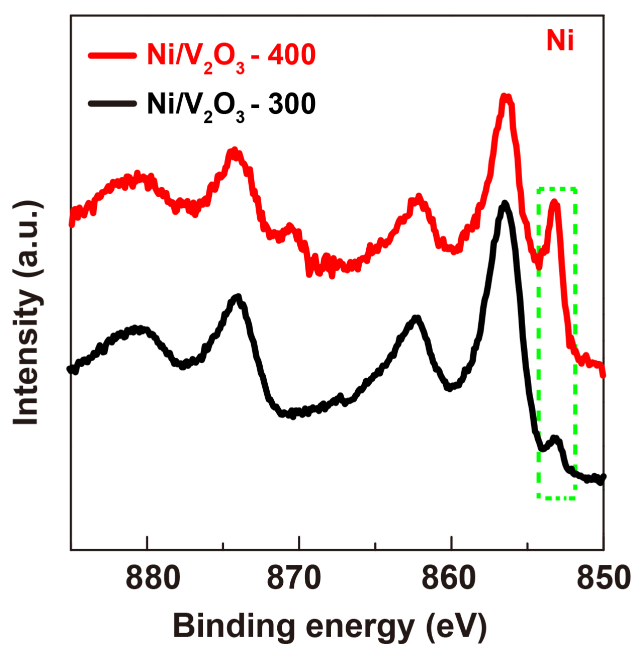

Fig. S11. Comparison of Ni 2p XPS spectra between Ni/V_2O_3-400 and Ni/V_2O_3-300.

As seen in this figure, the intensity of Ni^0 peak for Ni/V_2O_3-300 is much lower than Ni/V_2O_3-400, indicating the lower content of metallic Ni in the former which could be due to the incomplete decomposition of the precursor at 300 ºC.

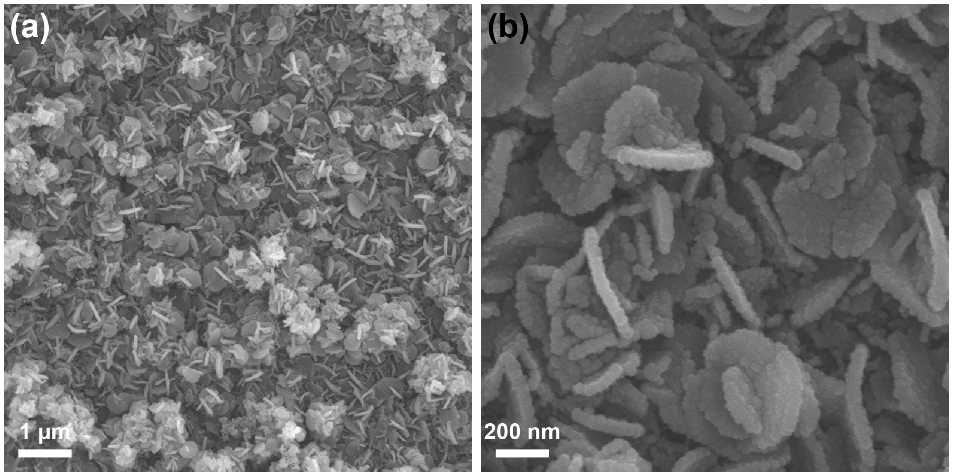

Fig. S12. (a-b) SEM images of Ni/V_2O_3 sample prepared using 0.4 mmol VCl_3.

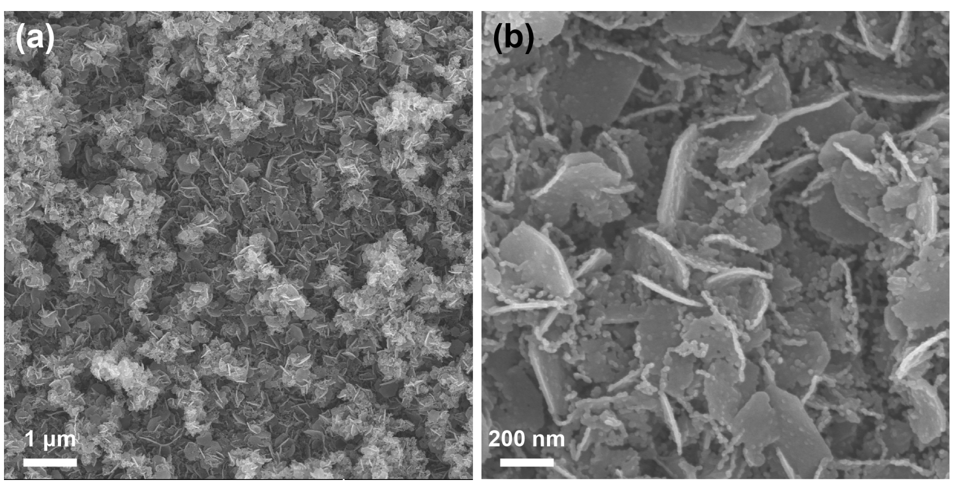

Fig. S13. (a-b) SEM images of Ni/V_2O_3 sample prepared using 0.8 mmol VCl_3.

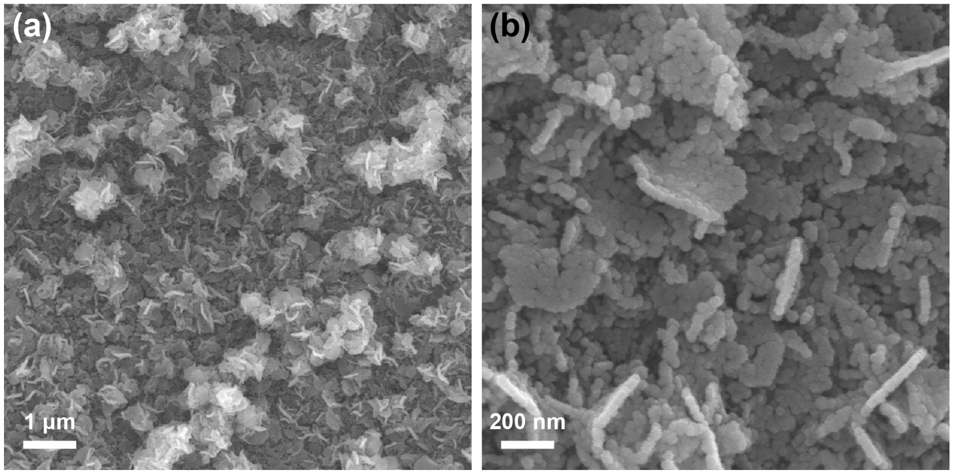

Fig. S14. (a-b) SEM images of Ni/V_2O_3 sample prepared using 1.2 mmol VCl_3.

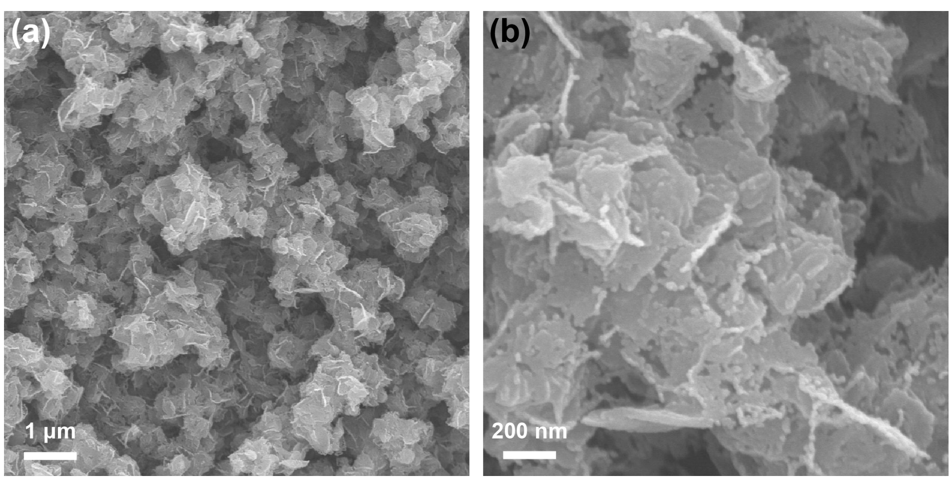

Fig. S15. (a-b) SEM images of Ni/V_2O_3 sample prepared using 2.0 mmol VCl_3.

Table S1. HER performance of recently reported Ni-based catalysts in 1 M KOH

Sample	**η@10 mA cm^{-2} [mV]**	**Tafel Slope [mV dec^{-1}]**	**Reference**
Ni/V_2O_3	61	79.7	**This Work**
NiO/Ni-CNT	＜100	82	*Nat. Commun.* **2014,** *5*, 4695
NiCu@C	74	94.5	*Adv. Energy Mater.* **2018** ,8, 1701759
Ni-Mn_3O_4	91	110	*Chem. Commun.* **2016**, *52*, 10566
NiSe/NF	96	120	*Angew. Chem. Int. Ed.* **2015**, 127, 9483
NiP/Ni	130	58.5	*Adv. Funct. Mater.* **2016**, 26, 3314
Ni-NiO/N-rGO	260	67	*Adv. Funct. Mater.* **2015**, 25, 5799
NiS_2 HMS	219	157	*J. Mater. Chem. A* **2017**, 5, 20985

Table S2. EIS results of different samples

Sample	R_s (Ω)	R_{ct} (Ω)
Ni/V_2O_3	1.87	4.27
Precursor	1.91	7.25
Ni foam	1.92	18.5
Mixed Ni+V_2O_3	2.89	8.09
Ni powder	2.91	15.4
V_2O_3 powder	2.95	31.4

Table S3. V/Ni ratios for Ni/V_2O_3 samples prepared using different amount of VCl_3

Samples prepared with different amount of VCl_3	V/Ni Ratio (XPS)
Ni/V_2O_3-0.4	1.33
Ni/V_2O_3-0.8	2.33
Ni/V_2O_3-1.2	3.55
Ni/V_2O_3-1.6	3.74
Ni/V_2O_3-2.0	4.00