

## Supporting Information

### **Efficient Coupling of Hierarchical V<sub>2</sub>O<sub>5</sub>@Ni<sub>3</sub>S<sub>2</sub> Hybrid Nanoarray for Pseudocapacitors and Hydrogen Production**

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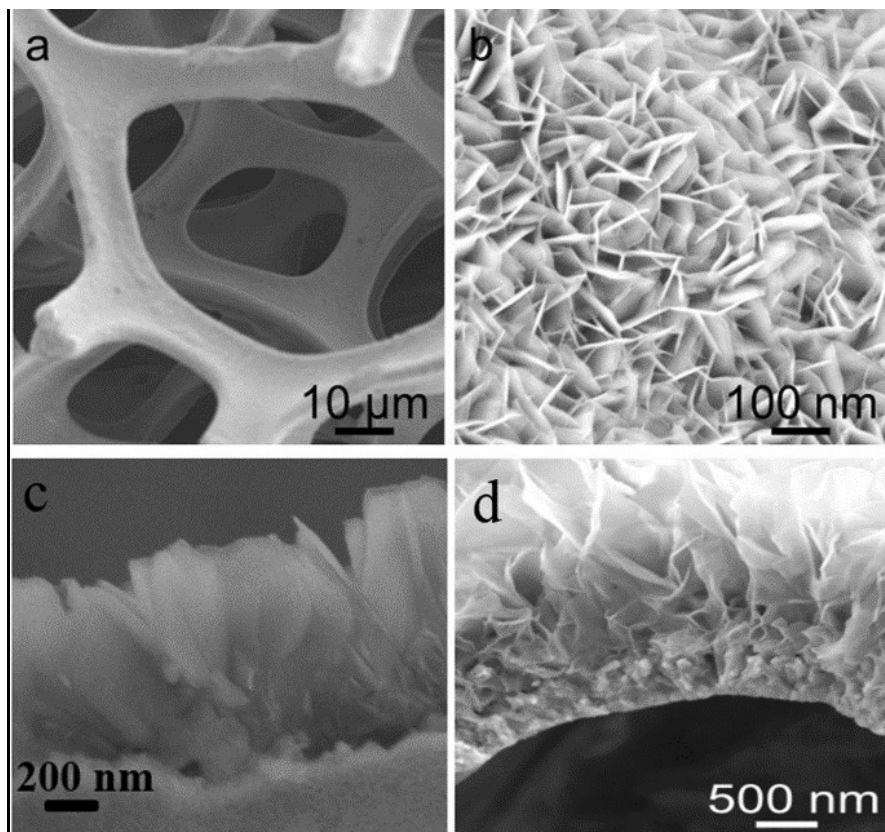


Figure S1. a) The top view, b) high-resolution, c) side view SEM images of a representative  $\text{Ni}_3\text{S}_2$  nanosheet, respectively. (d) A side view SEM image of  $\text{V}_2\text{O}_5@$   $\text{Ni}_3\text{S}_2$ .

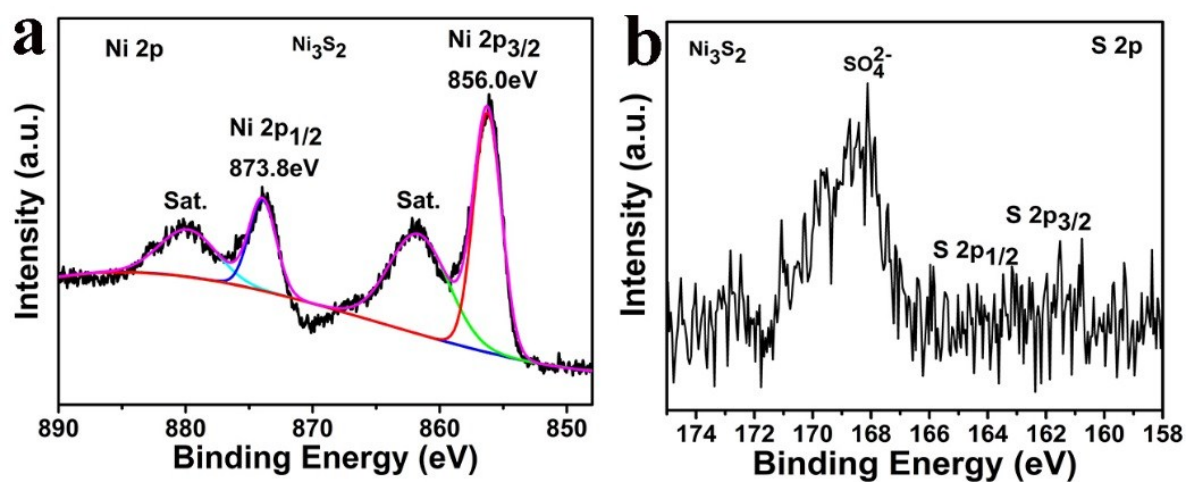


Figure S2. a) Ni 2p and b) S 2p XPS spectral peaks for  $\text{Ni}_3\text{S}_2$  nanosheet.

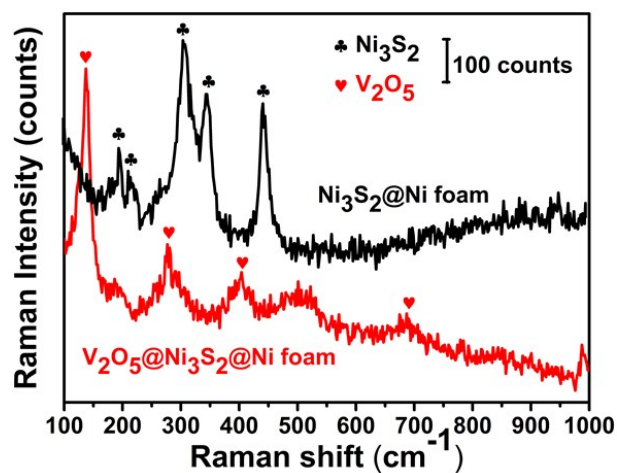


Figure S3. The Raman spectrum of  $\text{Ni}_3\text{S}_2$  (black) and  $\text{V}_2\text{O}_5@\text{Ni}_3\text{S}_2$  (blue) nanosheets.

From Figure S3, the Raman intensity of  $\text{Ni}_3\text{S}_2$  in the  $\text{V}_2\text{O}_5@\text{Ni}_3\text{S}_2$  sample is very low, and only strong  $\text{V}_2\text{O}_5$  can be detected. These results suggest the  $\text{V}_2\text{O}_5$  nanosheet completely cover  $\text{Ni}_3\text{S}_2$  nanosheet.

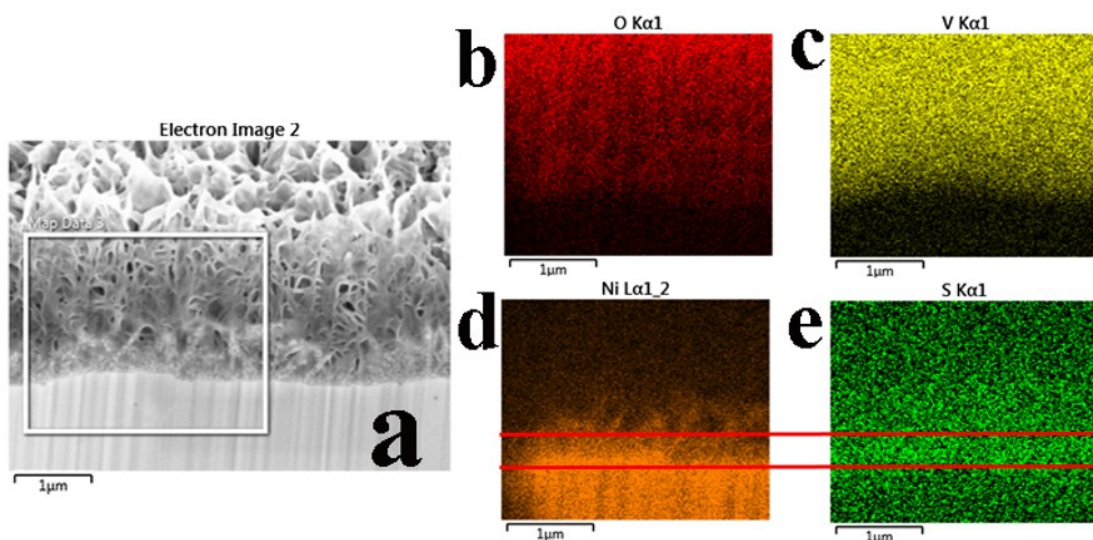


Figure S4. a) The SEM image showing the cross-section of  $\text{V}_2\text{O}_5@\text{Ni}_3\text{S}_2$ , using the FIB technique. The energy dispersive spectroscopy mapping of b) O, c) V, d) Ni and e) S,

and the region corresponding to a).

Figure S4 reveals that  $\text{V}_2\text{O}_5$  is on the top,  $\text{Ni}_3\text{S}_2$  in the middle and Ni foam at the bottom. The thicknesses of  $\text{V}_2\text{O}_5$  and  $\text{Ni}_3\text{S}_2$  layer are approximate  $2\ \mu\text{m}$  and  $0.4\ \mu\text{m}$ , respectively. The element dispersive mappings of Ni and S overlaps at the middle region, indicating this layer is  $\text{Ni}_3\text{S}_2$ .

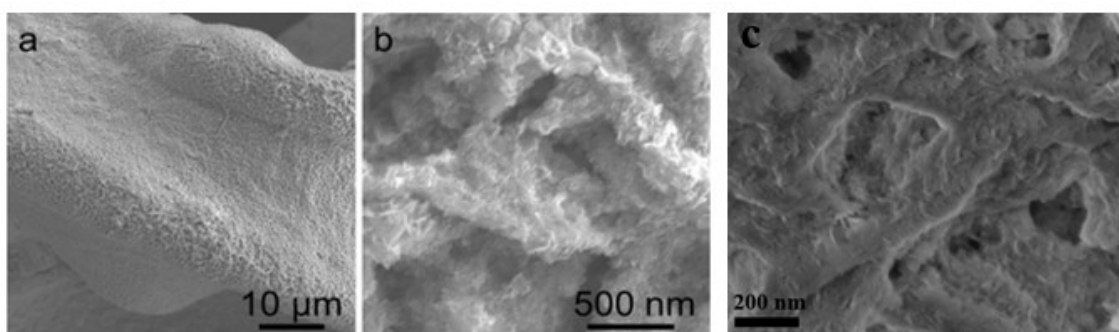


Figure S5. a) A top-view, b) a high-resolution SEM images of  $\text{V}_2\text{O}_5@ \text{Ni}_3\text{S}_2$  after 1000 galvanostatic charge/discharge (GCD) cycles. c) The SEM image of  $\text{Ni}_3\text{S}_2$  after 1000 GCD cycles.

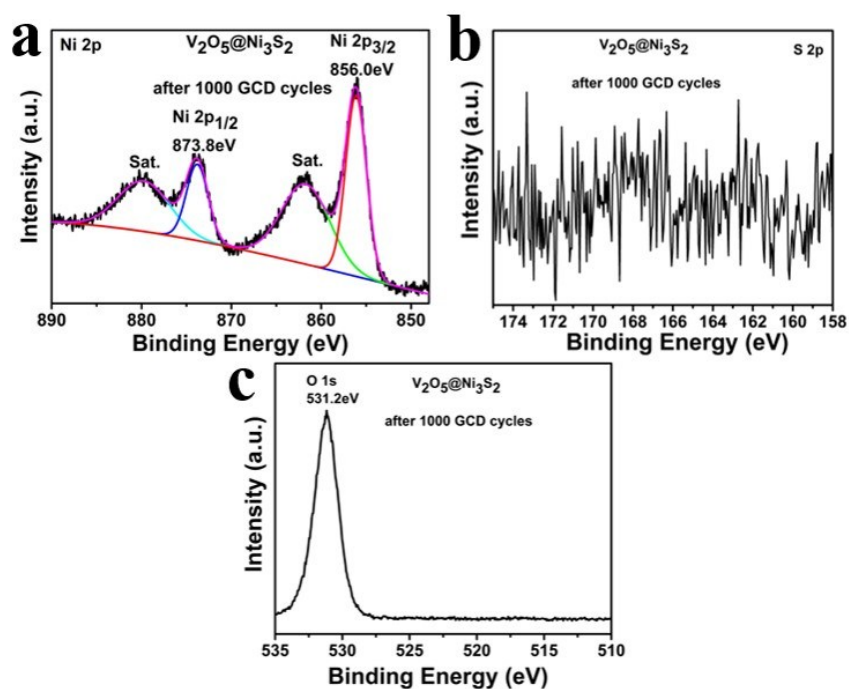


Figure S6. The a) Ni 2p, b) S 2p and c) O 1s XPS spectra of  $V_2O_5@Ni_3S_2$  after 1000 GCD cycles.

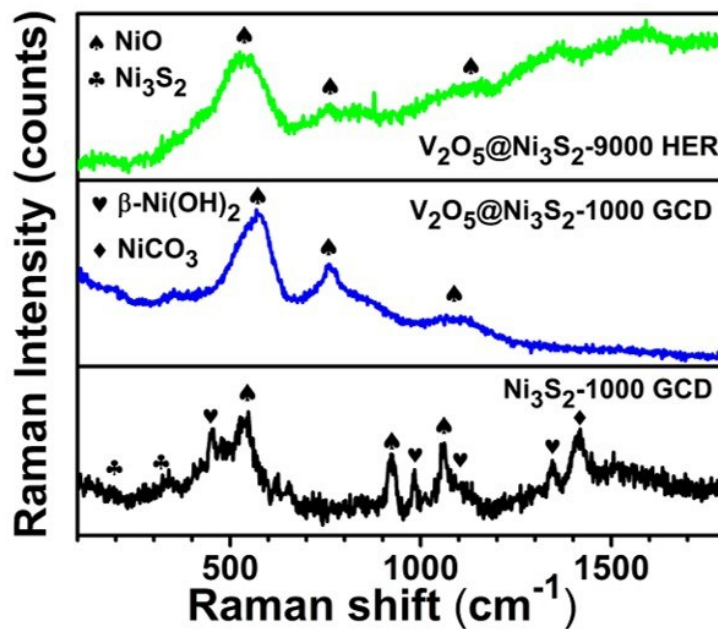


Figure S7. Raman spectra of  $Ni_3S_2$  after 1000 GCD cycles, and  $V_2O_5@Ni_3S_2$  after 1000 GCD cycles and 9000 linear sweep voltammetry (LSV) cycles, respectively.

The Raman spectroscopic investigation was conducted to identify the surface

chemical composition of  $\text{Ni}_3\text{S}_2$  and  $\text{V}_2\text{O}_5@\text{Ni}_3\text{S}_2$  after GCD and HER cycles, respectively. For  $\text{Ni}_3\text{S}_2$  after 1000 GCD cycles, the peak at  $545\text{ cm}^{-1}$  was attributed to one-phonon longitudinal optical (LO), the peak at  $923\text{ cm}^{-1}$  could be assigned to one-phonon transverse optical and one-phonon longitudinal optical mode (TO+LO), and the peak at  $1060\text{ cm}^{-1}$  was attributed to two-phonon longitudinal optical mode (2LO) mode. In addition, there are four peaks at  $453\text{ cm}^{-1}$ ,  $983\text{ cm}^{-1}$ ,  $1103\text{ cm}^{-1}$  and  $1347\text{ cm}^{-1}$  related to the  $\beta\text{-Ni(OH)}_2$  <sup>3-5</sup>, two peaks at  $196\text{ cm}^{-1}$  and  $320\text{ cm}^{-1}$  related to the  $\text{Ni}_3\text{S}_2$  <sup>6</sup> and one peak at  $1416\text{ cm}^{-1}$  corresponded to  $\text{NiCO}_3$  <sup>7</sup>. It reveals that the  $\text{V}_2\text{O}_5$  grown on  $\text{Ni}_3\text{S}_2$  which can be efficiently impeded  $\text{Ni}_3\text{S}_2$  corrosion and produced to  $\beta\text{-Ni(OH)}_2$  and the  $\beta\text{-Ni(OH)}_2$  maybe reacted with carbon oxide from air to form  $\text{NiCO}_3$ .

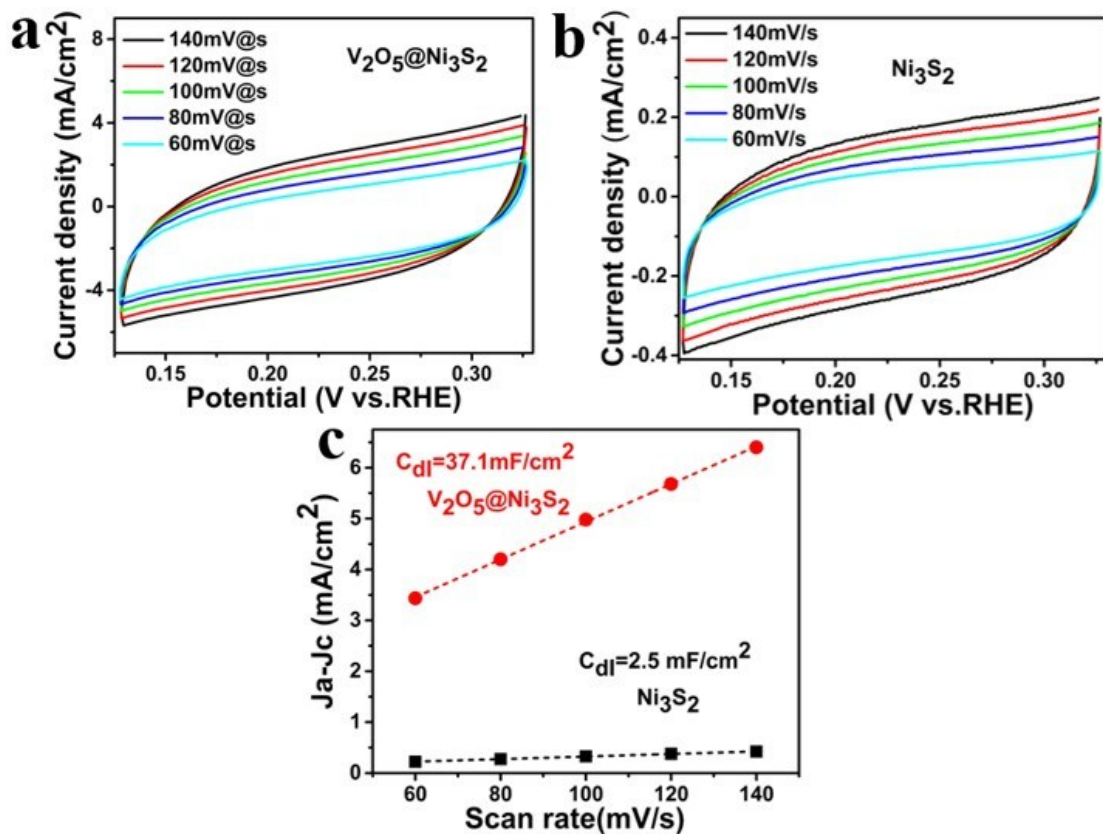


Figure S8. a), b) Cyclic voltammograms (CVs) at different scan rate in the region of 0.13V~0.32 V (vs. RHE) for  $V_2O_5@Ni_3S_2$  and  $Ni_3S_2$ , respectively. c) The variation of double-layer charging currents of  $V_2O_5@Ni_3S_2$  and  $Ni_3S_2$  at 0.225 V (vs. RHE) under various scan rates, respectively.



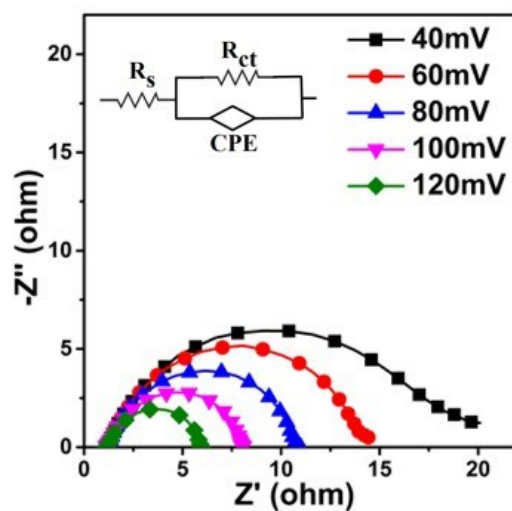


Figure S9. Nyquist plots of  $\text{V}_2\text{O}_5@\text{Ni}_3\text{S}_2$  at various HER overpotentials.

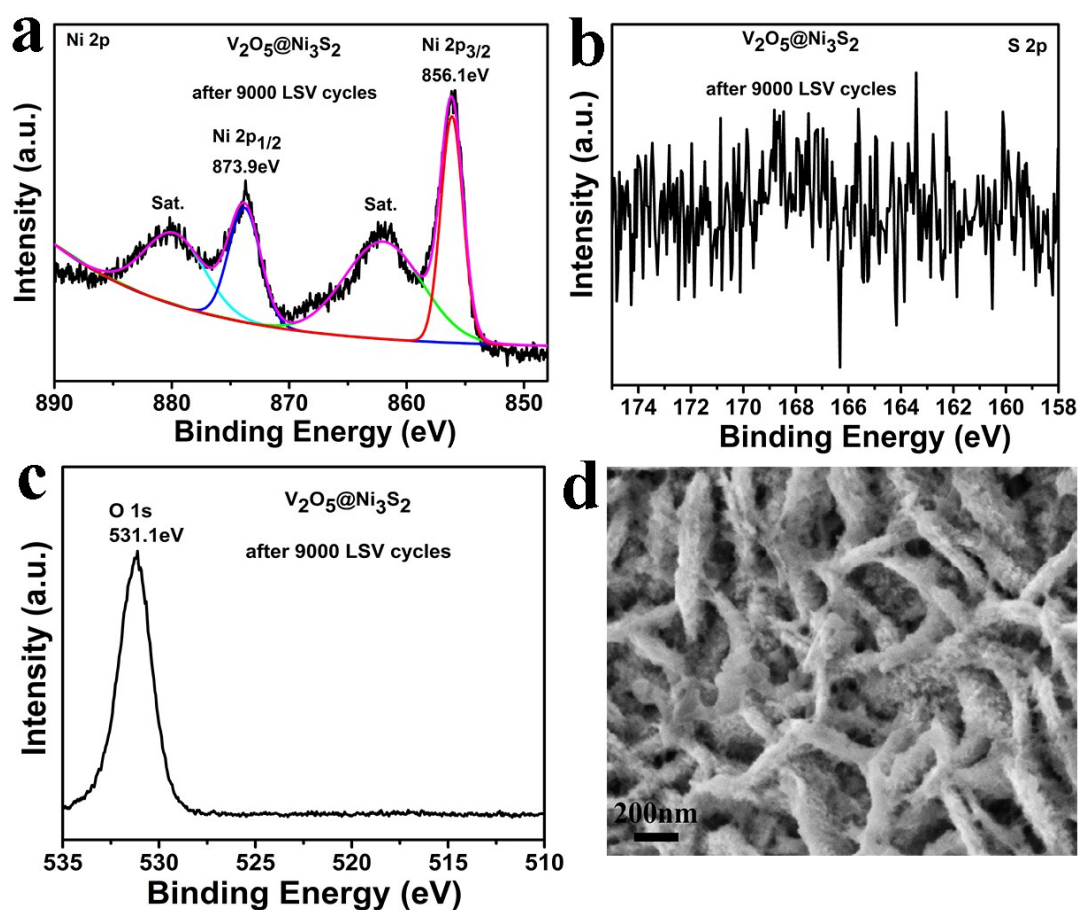


Figure S10. The XPS spectra of Ni 2p a), S 2p b) and O 1s c). d) High-resolution SEM image of  $\text{V}_2\text{O}_5@\text{Ni}_3\text{S}_2$  after 9000 LSV cycles.



## References

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