Supporting Information

Ni_3S_2/Ni Nanosheets Arrays for High-performance Flexible Zinc Hybrid Battery with Evident Two-stage Charge and Discharge Process

*Zhaodong Huang, Xinliang Li, Qi Yang, Longtao Ma, Funian Mo, Guojin Liang, Donghong Wang, Zhuoxin Liu, Hongfei Li, Chunyi Zhi**

Department of Materials Science and Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong SAR, China

** E-mail: c.y.zhi@cityu.edu.hk*

Experimental

Materials synthesis

Preparation of Ni_3S_2 nanosheets: The Ni_3S_2 nanosheets was prepared through

hydrothermal method with Ni foam, thiourea and sucrose serving as Ni, S and C sources, respectively. Typically, 2.35 g thiourea was dissolved in 80 ml deionized water, followed with 2.35 g Ni foam added. Then, the solution was transformed into a Teflon-lined stainless-steel autoclave with a capacity of 100 mL. The autoclave was sealed and placed in an oven at 150 °C for 5 h, followed by cooling to room temperature in air for several hours. The obtained flakey products were washed with deionized water and ethyl alcohol for several times and then dried at 80 °C for 24 h under vacuum oven. The obtained product was named as Ni_3S_2-1.0. For comparison, different additive amounts of thiourea (1.175 and 3.525 g) were reacted with 2.35 g Ni foam in the same condition, and the products were denoted as Ni_3S_2-0.5 and Ni_3S_2-1.5, correspondingly.

Preparation of PANa hydrogel: Acrylic acid, Ammonium persulphate, N, N'-methylene diacrylamide were utilized as monomer, initiator, crosslinker, respectively. Specifically, 7.2 ml acrylic acid was mixed with 10 ml deionized water to form solution A. 4 g NaOH was dissolved in 10 ml deionized water to form solution B. The solution B was added into solution A dropwise with stirring and ice-bath cooling. Then, 110mg ammonium persulphate was added into the mixed solution, followed with 4 mg N, N'-methylene diacrylamide added. Subsequently, the solution was the solution was placed in an oven at 65 °C for 2 h to allow free-radical polymerization. Finally, the hydrogel will be soaked in the mixture solution of potassium hydroxide and zinc acetate, which will be the electrolyte for the hybrid battery.

2.2 Materials characterization

The morphology, structure and composition of Ni_3S_2 in different ratio were examined by scanning electron microscopy (SEM, FEI Quanta 450 FEG), transmission electron microscopy (TEM, JEOL-2001F) and thermogravimetric analysis (TGA, NETZSCH STA449F3), and the interlayer spacing was investigated by SAED. XRD patterns were recorded with Cu Kα radiation (λ=0.15418 nm) at 30 kV and 10 Ma using Bruker D2 Phaser to study the composition

and crystalline structure during the electrochemical discharge/charge processes. The surface chemical state of Ni and S were monitored by XPS (ESCALAB 250 photoelectron Page 23 of 29 Energy & Environmental Science spectroscopy) to get an insight into the activation of Ni_3S_2 cathode.

2.3 Electrochemical properties

The as-prepared Ni_3S_2 was directly utilized as cathode materials, and zinc plate, 6 M KOH solution with 0.2 M $Zn(Ac)_2$ additive were adopted as anode and electrolyte. CV and GCD of as assembled batteries were tested by a CHI 760E potentiostat. All these were conducted at ambient conditions.

Fabrication of flexible hybrid ZAMB: The Zn anode was prepared by electrodeposition on a carbon cloth (width: 1 cm; length: 5 cm; thickness: 400 mm; resistivity: 0.1 mW cm^2) at -0.8V vs. Zn foil for 5 min in zinc sulfate (1 M). The as-prepared Ni_3S_2 was served as cathode. The anode and cathode were paved on the PANa film electrolyte (thickness: 1.5 mm), which also served as a separator.

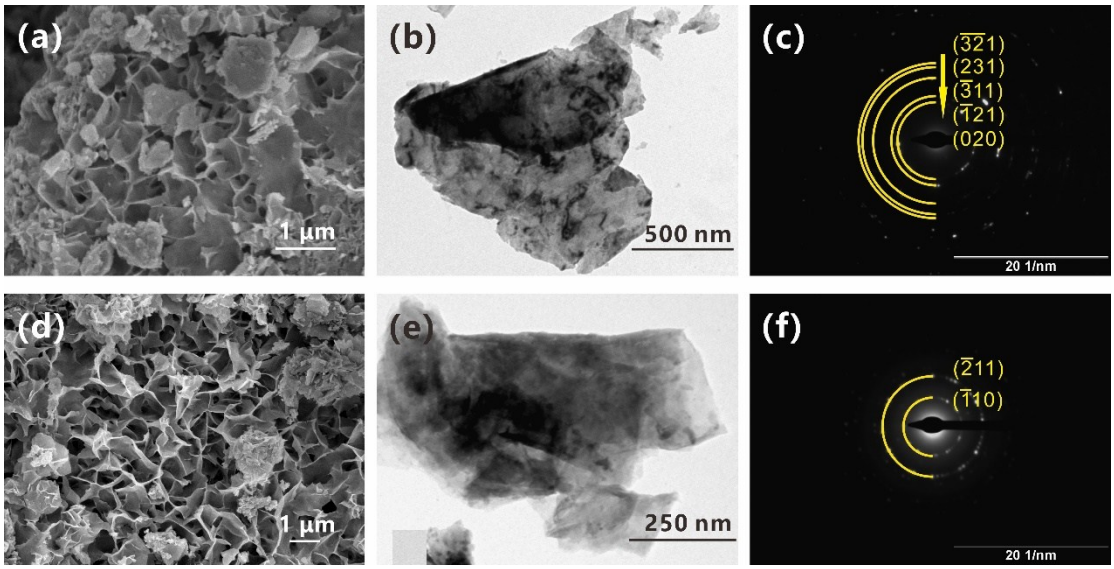

Figure S1. SEM (a, d), TEM (b, e) and SAED (c, f) images of Ni_3S_2-0.5 and Ni_3S_2-1.5, respectively.

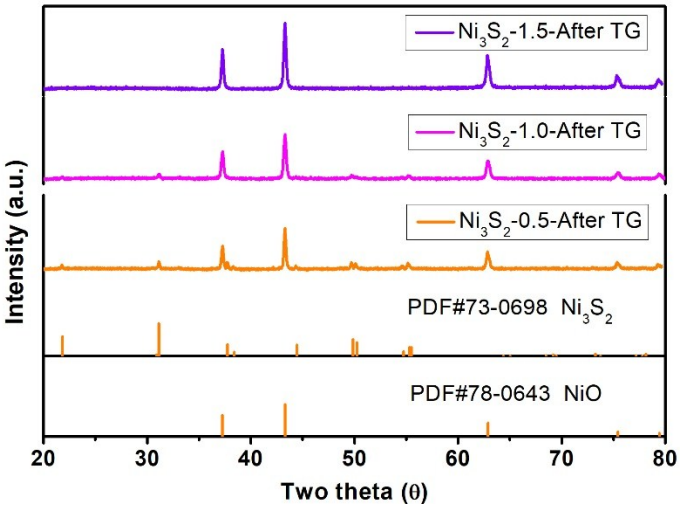

Figure S2. XRD patterns after TG measurement of Ni_3S_2-0.5, Ni_3S_2-1.0 and Ni_3S_2-1.5.

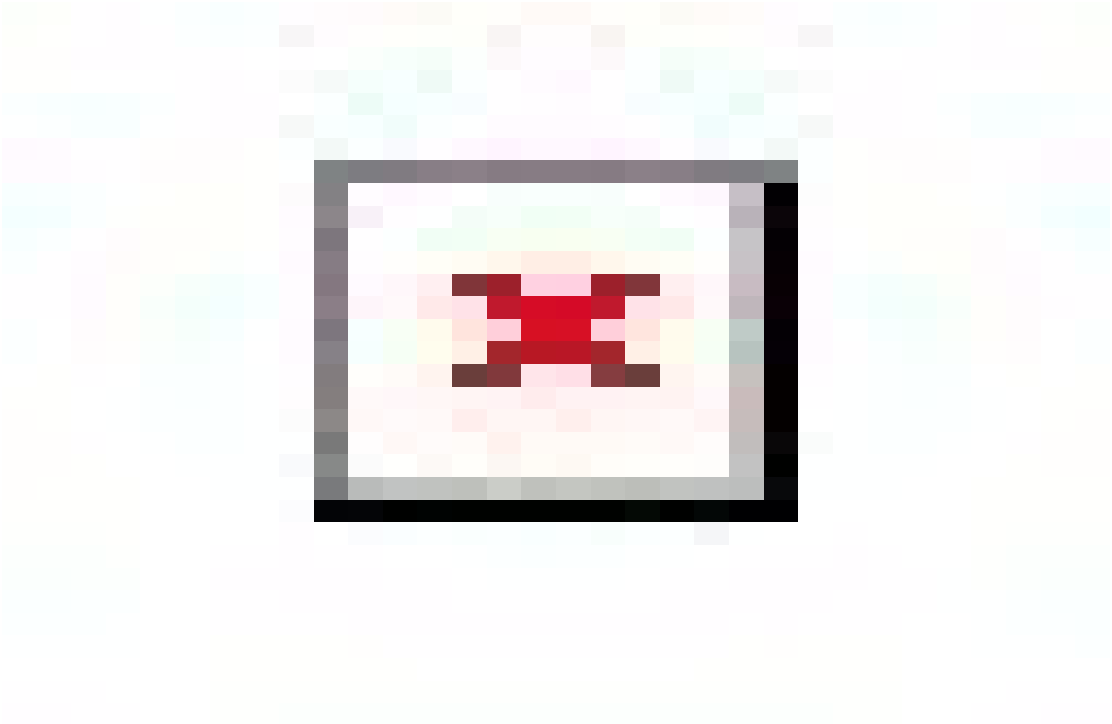

Figure S3. XRD patterns (a, c) and partial enlarged details (b, d) in different state of Ni_3S_2-0.5 and Ni_3S_2-1.5, respectively.

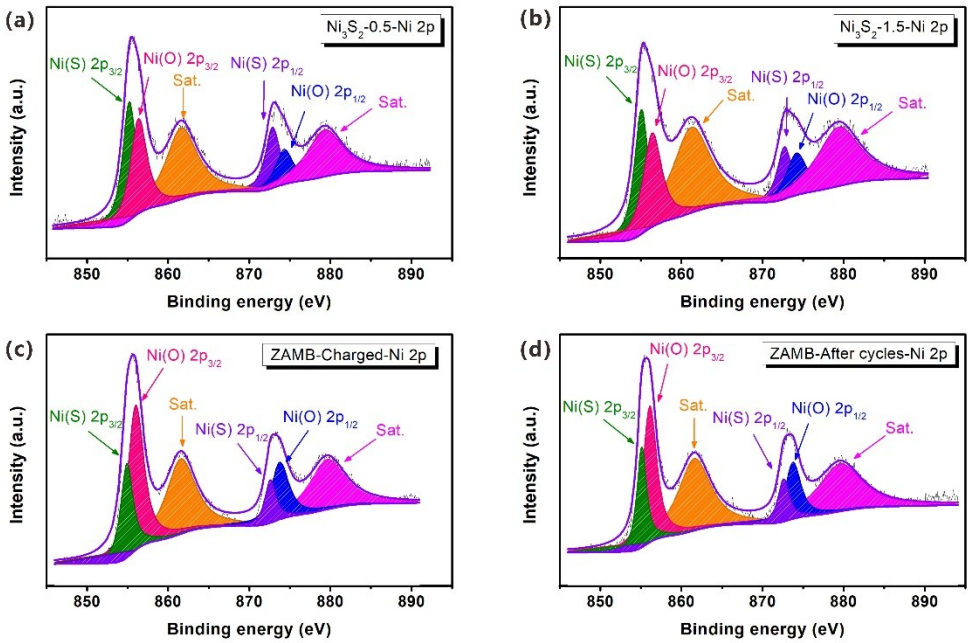

Figure S4. High resolution Ni 2p spectrum of Ni_3S_2-0.5 (a), Ni_3S_2-1.5 (b) in the initial state; High resolution Ni 2p spectrum of Ni_3S_2-1.0 for ZAMB in charged-state (c) and after 100 cycles state (d).

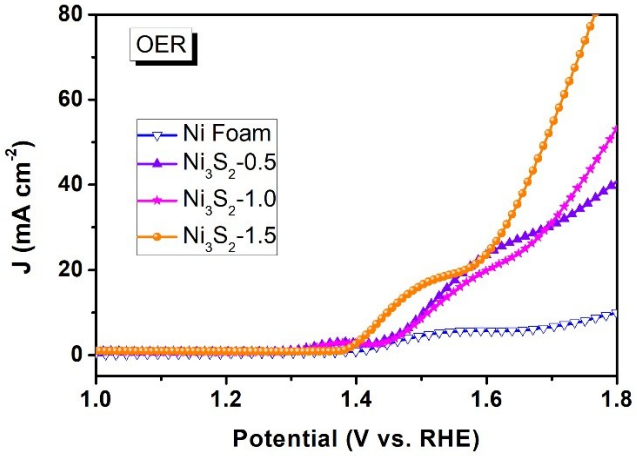

Figure S5. The OER catalytic activity of Ni foam, Ni_3S_2-0.5, Ni_3S_2-1.0 and Ni_3S_2-1.5.

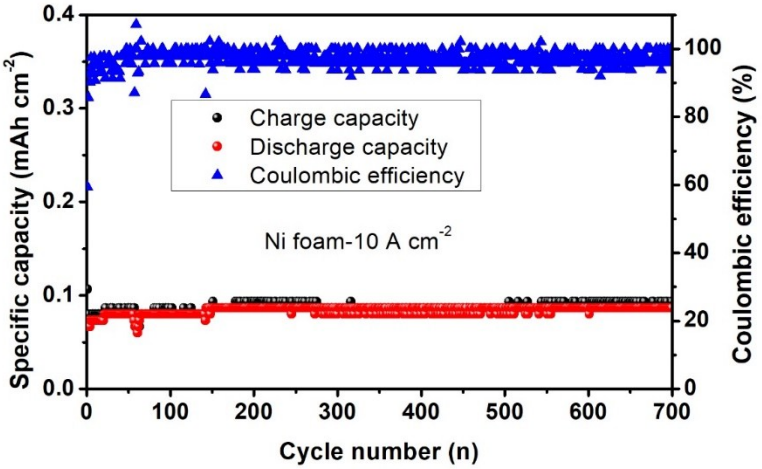

Figure S6. The electrochemical performance of Ni foam cycling at a current density of 10 A cm^{-2}.

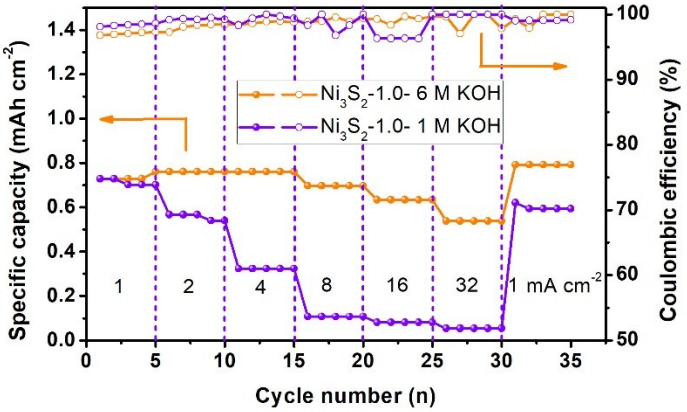

Figure S7. The rate capabilities comparison of Ni_3S_2-1.0 in 6 M KOH and 1 M KOH electrolyte.

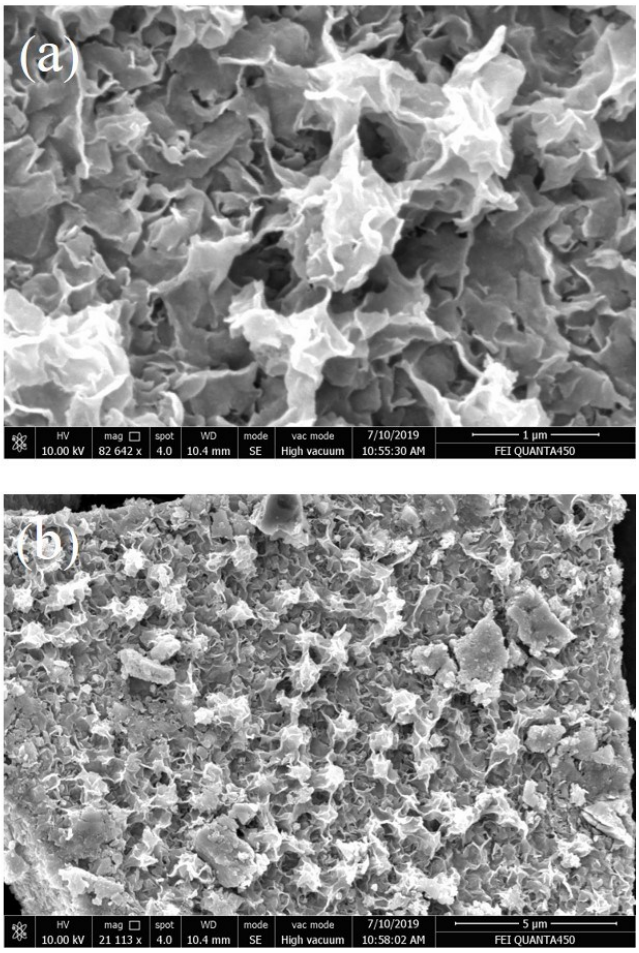

Figure S8. SEM images of Ni3S2 after 600 cycles at a current density of 10 A cm^{-2}

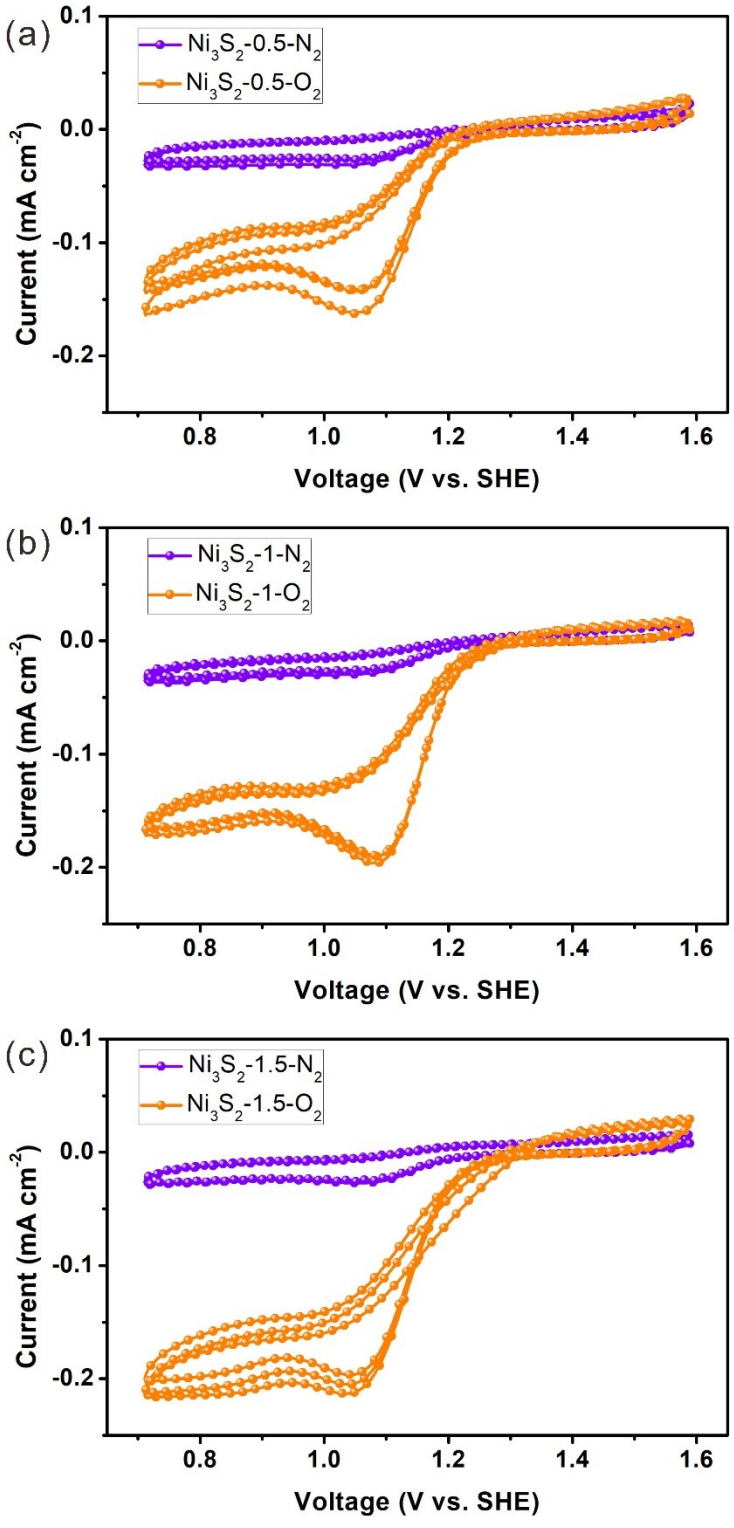

Figure S9. The three-electrode CV curves of Ni_3S_2-0.5, Ni_3S_2-1.0 and Ni_3S_2-1.5 with or without oxygen exist.

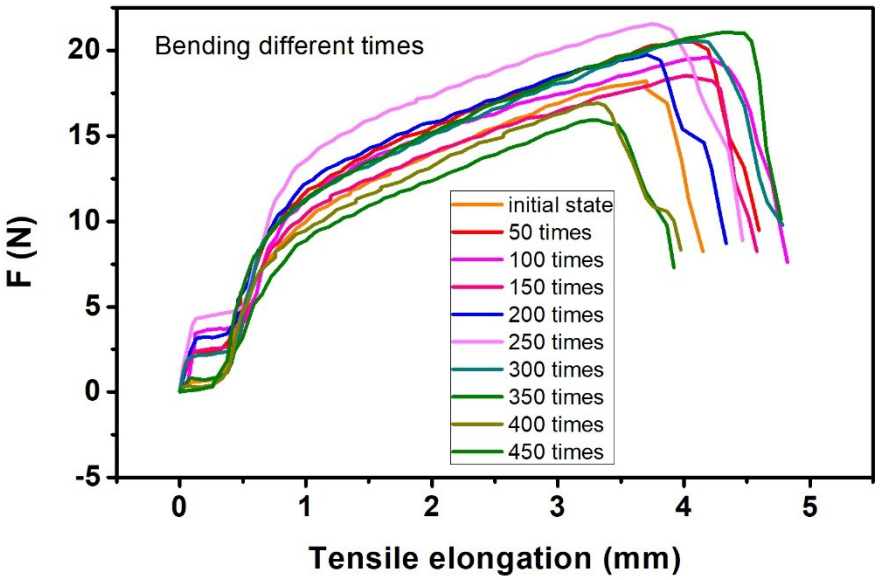

Figure S10. Tension test of Ni_3S_2-1.0 film after different bending times