Electronic Supplementary Information

Rigid Three-Dimensional Ni_3S_4 Nanosheet Frames: Controlled Synthesis and Their Enhanced Electrochemical Performance

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I. Materials and Methods

Chemicals. $NiCl_2 \cdot 6H_2O$ (98%), sodium stearate (90%), potassium hydroxide were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Oleic acid (OA) was purchased from Aladdin Ltd. (Shanghai, China). N-dodecanethiol (DDT) (98%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Methanol, ethanol, toluene, and hexane were purchased from Beijing Chemical Works (Beijing, China). All materials were analytical grade used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Synthesis of nickel sulfide nanostructures

(1) **Nickel stearate was used as Ni source.** In a typical procedure, 0.25 mmol $NiCl_2 \cdot 6H_2O$ and 0.5 mmol of sodium stearate were dissolved in a mixture solvent composed of 1.3 mL distilled water, 5mL methanol, 7 mL hexane, heated to 60 ^oC for 4h. The upper organic layer containing nickel sterarate ($NiSt_2$) were decanted and washed for several times with ethanol by centrifuge. The deposit was finally re-dispersed in 0.33ml hexane.

(2) **Synthesis of 3D Ni_3S_4 nanosheet frames**: in a typical procedure, 6ml as-prepared $NiSt_2$ hexane solution, and 0.5 ml DDT were all added into 6ml OA at room temperature. After continuous stirring for 5min, the mixed solution was transferred into a Teflon-lined stainless steel autoclave with 10 ml capacity and maintained at 200 ^oC for 2.5h. Finally, the solution was cooled down to room temperature naturally, and the mixture was centrifuged to isolate a black precipitate which was washed with ethanol until the supernatant became clear. Then the as-prepared 3D Ni_3S_4 nanosheet frames were re-dispersed in ethanol for further characterization.

(3) **Synthesis of Ni_3S_4 sheet:** The experimental parameters to prepare Ni_3S_4 sheet were as same as that of synthesizing 3D Ni_3S_4 nanosheet frames above, except that DDT was increasing to 1mL. The final products were also isolated by centrifugation and could be well re-suspended in ethanol for further characterization.

(4) **Control experiments**: To investigate the evolution of flat Ni_3S_4 sheets to 3D

Ni_3S_4 nanosheet frames, controlled experiments were designed by varying the DDT concentration (0.6, 0.8 ml) or the reaction time (0.5, 1.0, 1.5, 2.0 h) while keeping other experimental parameters unchanged.

Characterizations The morphologies of the as-synthesized nickel sulfide nanostructure were examined on JEOL JEM-1200EX transmission electron microscope (TEM) (Hitachi H-7650B) at 100.0 kV. High resolution TEM was recorded on Tecnai G2 F20 S-Twin, operating at 200.0 kV. Field emission scanning electron microscopy (FESEM) was carried out on a SIRION 200. The thickness of the Ni_3S_4 sheet was qualified by a Dimension 3100 AFM system (Bruker, USA) under ambient condition. Commercial silicon tips with resonant frequency of 275.4 kHz are used in all the AFM imaging. The TEM, HRTEM, AFM sampling are prepared by dropping the ethanol containing nickel sulfide nanostructure onto the copper grid, holey carbon grid, and mica respectively, which are then being dried naturally under ambient condition. X-ray diffraction (XRD) patterns of the as-obtained product were recorded on a Bruker D8 Advance powder X-ray diffractometer at a scanning rate of 2^o min^{-1}, using Cu-Kα radiation (λ=1.5406 Å). Measurements of specific surface area and porosity were carried out at 77K with a Quantachrome Instrument ASiQMVH002-5 system.

Electrochemical measurements

Electrochemical study on nickel sulfide nanostructured electrodes was carried out on a CHI660E electrochemical working station (Shanghai Chenhua Instrument, Inc.). All electrochemical performances were carried out in a conventional three-electrode system equipped with platinum electrode and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. The working electrode was made by mixing active materials (nickel sulfide nanomaterials), acetylene black, and polytetrafluoroethelyene (PTFE) with a weight ratio of 85:10:5, coated on a piece of foamed nickel foam of about 1 cm^2, and pressed to be thin foil at the pressure of 5.0 MPa. The electrolyte was a 3.0 M KOH solution. Cyclic voltammetry and galvanostatic charge-discharge methods were used to investigate capacitive properties of nickel sulfide nanostructured electrodes. The cycling tests of the electrodes were performed using charge and discharge cutoff voltage of 0-0.4 V on LAND CT 2001A. All performances were tested at room temperature.

II. Supporting figures

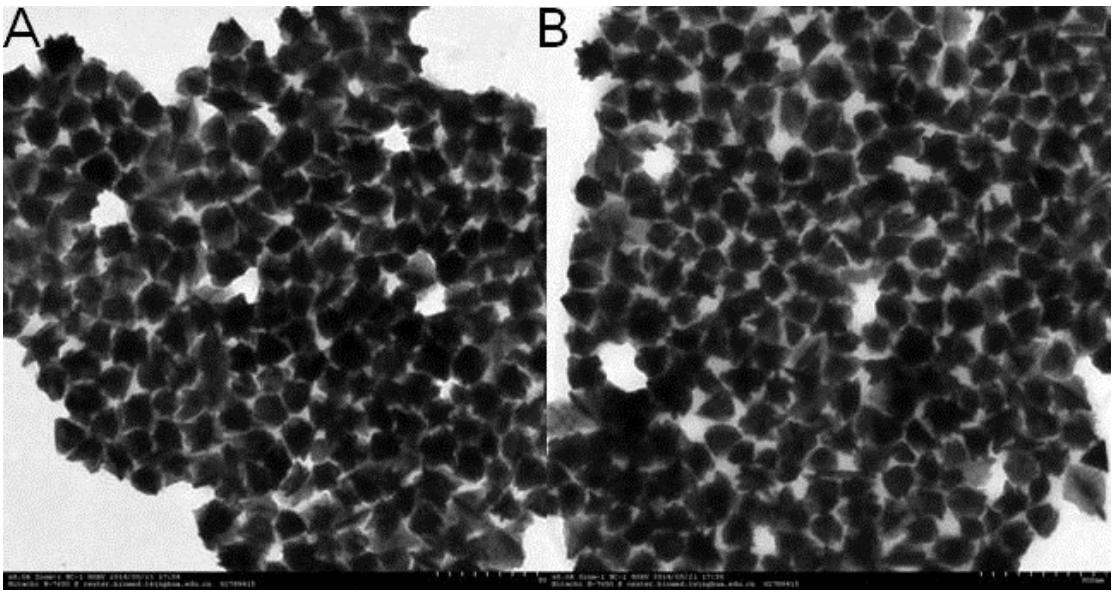

Fig. S1 TEM images of the 3D Ni_3S_4 nanosheet frames after 30 min of ultrasonication. No obvious morphology changes for the 3D Ni_3S_4 nanosheet frames were observed, indicative of the high rigidity of the as-prepared products. The power of the ultrasound was set at 100 W 42 kHz (Bransonic® ultrasonic cleaner).

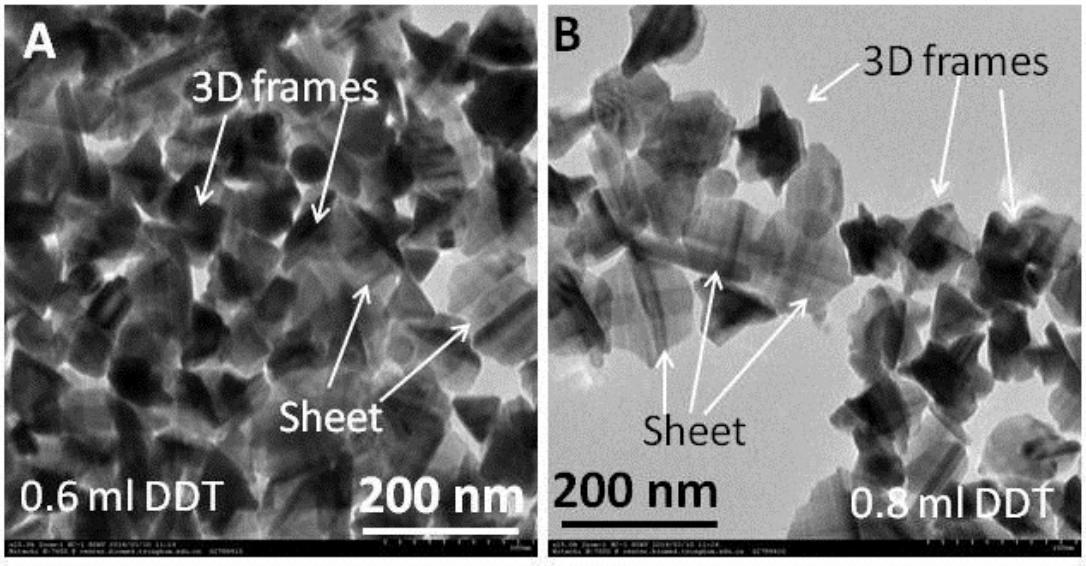

Fig. S2 TEM images of the morphology evolution of Ni_3S_4 nanostructure (A) DDT concentration is 0.6 ml, (B) DDT concentration is 0.8 ml. From TEM images, it can be seen that at the medium DDT concentration (0.6 ml and 0.8 ml), the final product is composed of both sheets and 3D frames.

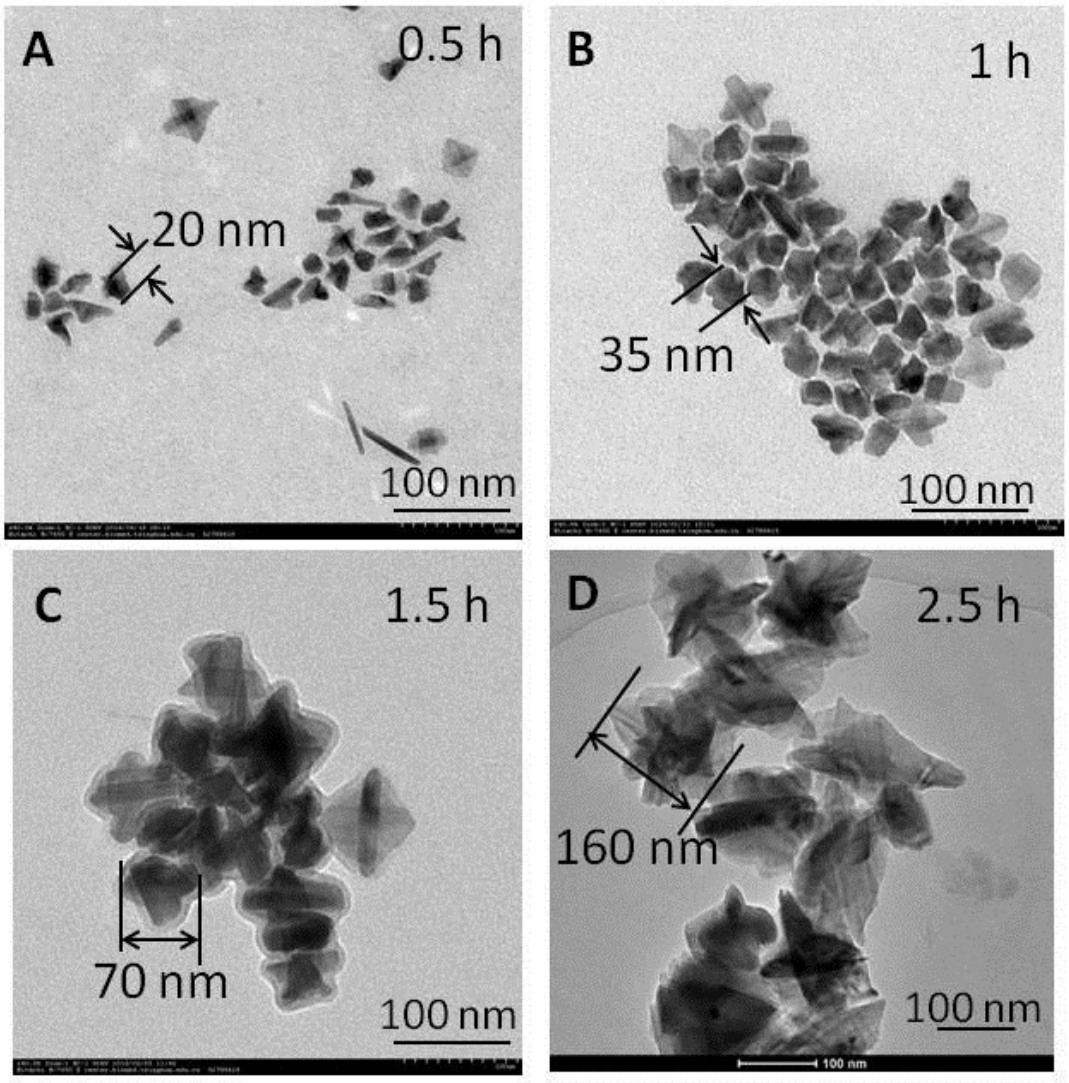

Fig. S3 TEM images of the morphology evolution at different time intervals of the as-prepared 3D Ni_3S_4 nanosheet frames. (A) 0.5h, (B) 1h, (C) 1.5h, (D) 2.5h.

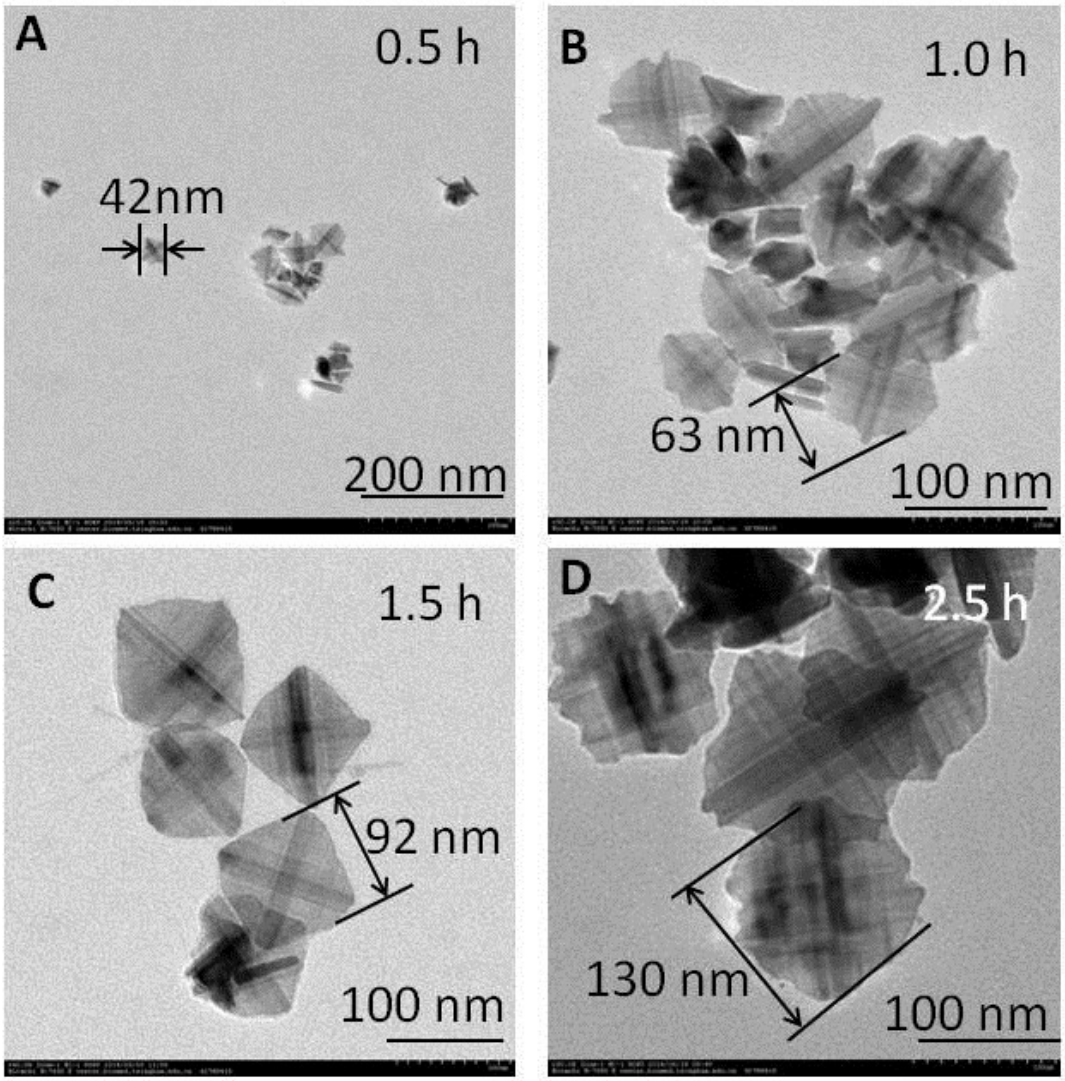

Fig. S4 TEM images of the morphology evolution at different time intervals of the as-prepared Ni_3S_4 sheets. (A)0.5 h, (B) 1.0 h, (C) 1.5 h, (D) 2.5h.

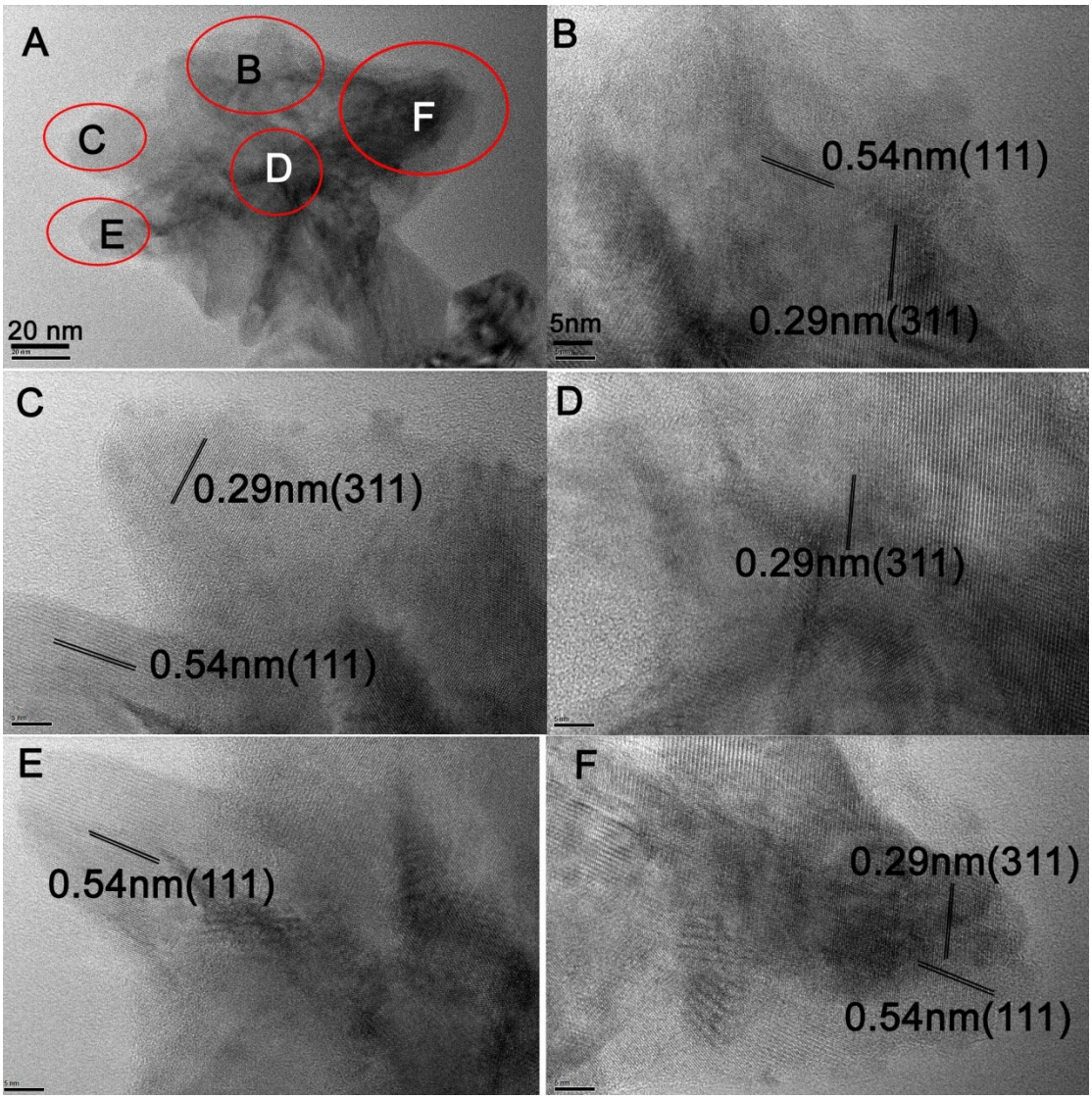

Fig. S5 HRTEM images of the morphology of the as-prepared 3D Ni_3S_4 nanosheet frames. (A) HRTEM image of a single 3D Ni_3S_4 nanosheet frames. (B) HRTEM image of the circled region B shown in panel A. The lattice fringes have a measured *d* spacing of ～0.54 nm, ～0.29 nm and should correspond to the (111), (311) planes of Ni_3S_4. (C) HRTEM image of the circled region C shown in panel A. The lattice fringes have a measured *d* spacing of ～0.54 nm, ～0.29 nm and should correspond to the (111), (311) planes of Ni_3S_4. (D) HRTEM image of the circled region D shown in panel A. The lattice fringes have a measured *d* spacing of ～0.29 nm and should correspond to the (311) planes of Ni_3S_4. (E) HRTEM image of the circled region E shown in panel A. The lattice fringes have a measured *d* spacing of ～0.54 nm and should correspond to the (111) planes of Ni_3S_4. (F) HRTEM image of the circled region F shown in panel A. The lattice fringes have a measured *d* spacing of ～0.54 nm, ～0.29 nm and should correspond to the (111), (311) planes of Ni_3S_4.

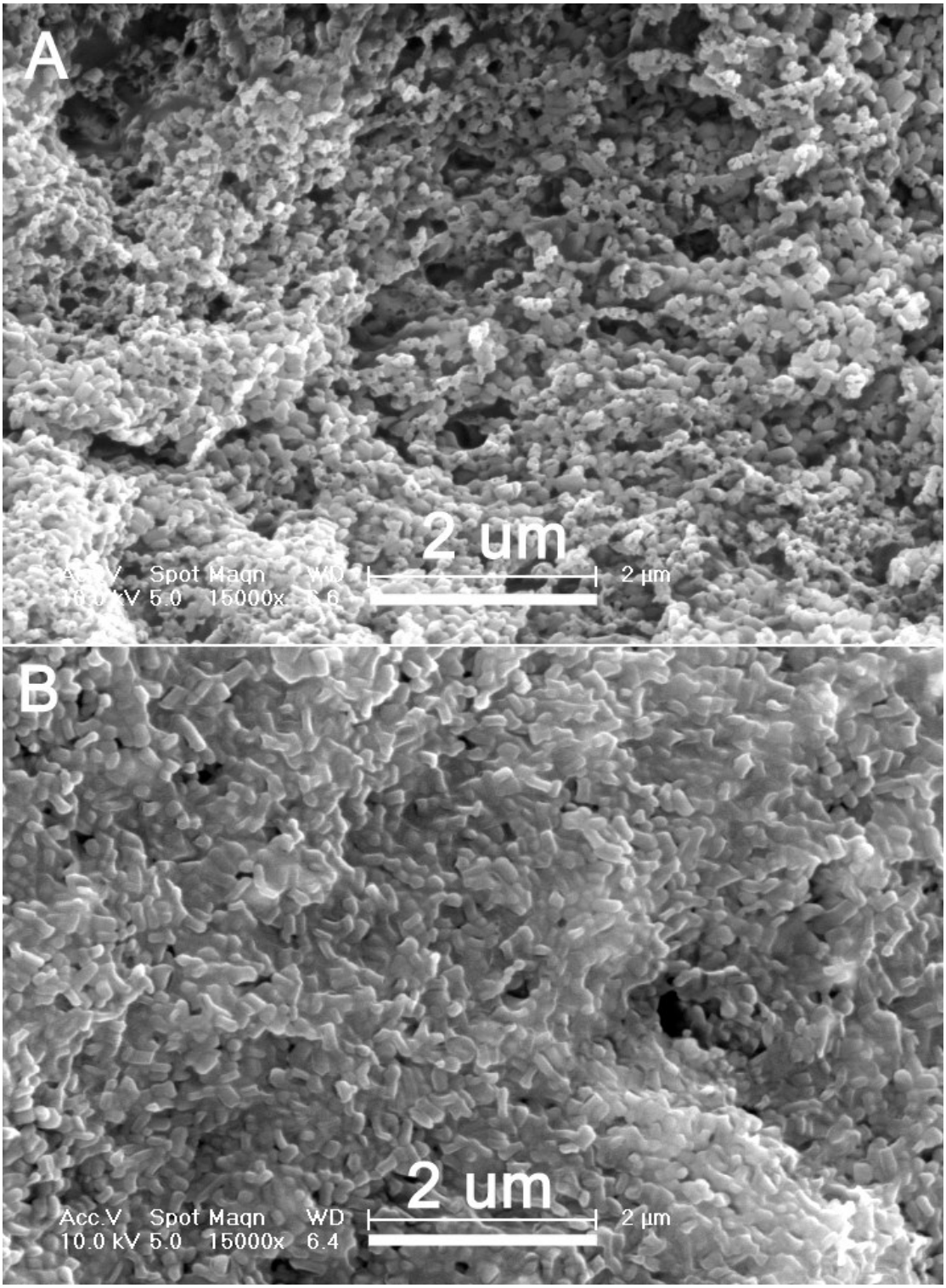

Fig. S6 SEM images of the 3D Ni_3S_4 nanosheet frames (A) and Ni_3S_4 nanosheet (B) electrodes after pressing.

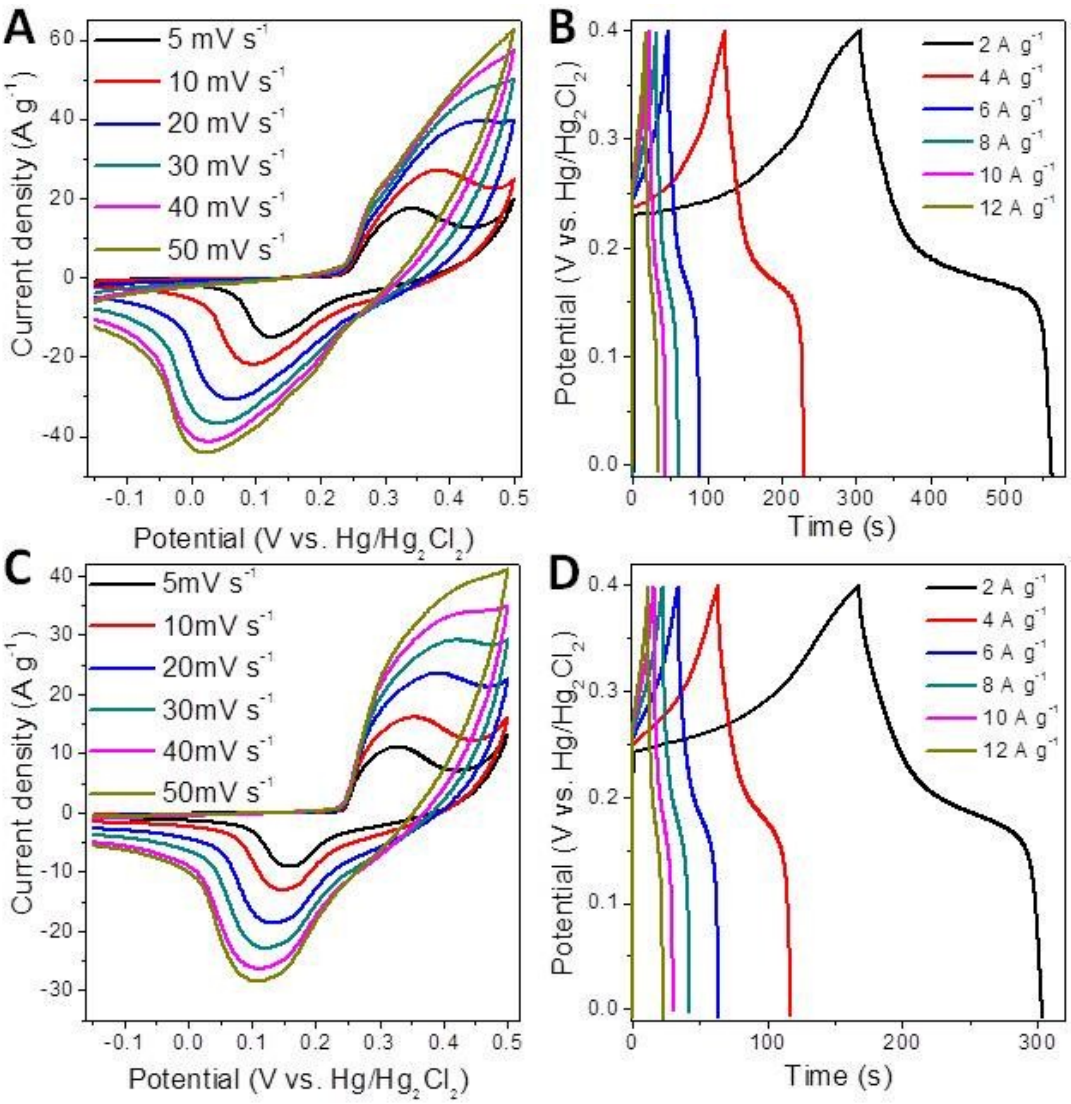

Fig. S7 (A, C) CV curves in the range of -0.15-0.5 V at various scan rates of the 3D Ni_3S_4 nanosheet frame electrode, and the flat Ni_3S_4 sheet electrode, respectively, (B, D) galvanostatic charge-discharge curves at various current density in the range of 0-0.4 V of the 3D Ni_3S_4 nanosheet frame electrode, and the flat Ni_3S_4 sheet electrode, respectively.