Supplementary information

Two dimensional mesoporous Co_3S_4 nanosheets as promising anode for Li-ion battery and bi-functional electro-catalyst for Li-O_2 systems

Palanichamy Sennu[a], Maria Christy[b], Vanchiappan Aravindan[c], Young-GiLee[d], Kee Suk Nahm[b] and Yun-Sung Lee*[a]*

[a]Faculty of Applied Chemical Engineering, Chonnam National University, Gwang-ju 500-757, Republic of Korea

[b]R&D Education Centre for Fuel Cell Materials & Systems, Chonbuk National University, Jeonju 561-756, Republic of Korea.

[c]Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Research Techno Plaza, 50 Nanyang Drive, Singapore 637553

[d]Power Control Device Research Team, Electronics and Telecommunications Research Institute, Daejeon 305-700, Korea

Preparation of Co_3O_4 nanosheets

The conventional hydrothermal route was employed to prepare the large-area hierarchical mesoporous Co_3O_4-NS with simple and cost-effective manner. In a typical process, 1g $CoCl_2.6H_2O$ (Wako, Japan) and 4g urea (Junsei, Japan) were dissolved in 70 mL distilled water by intense stirring for 10 minutes. Then, 1g of Polyvinylpyrrolidone (M_W = 40,000, Sigma-Aldrich, USA) was added to the transparent pink solution, which was then, stirred for 1 h at room temperature. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave and heated to 120 °C for 24h. The precipitate was filtered and washed with water and ethanol several times. Finally, the products were calcined at 400 °C for 3 h in a tube furnace to yield the desired Co_3O_4-NS.

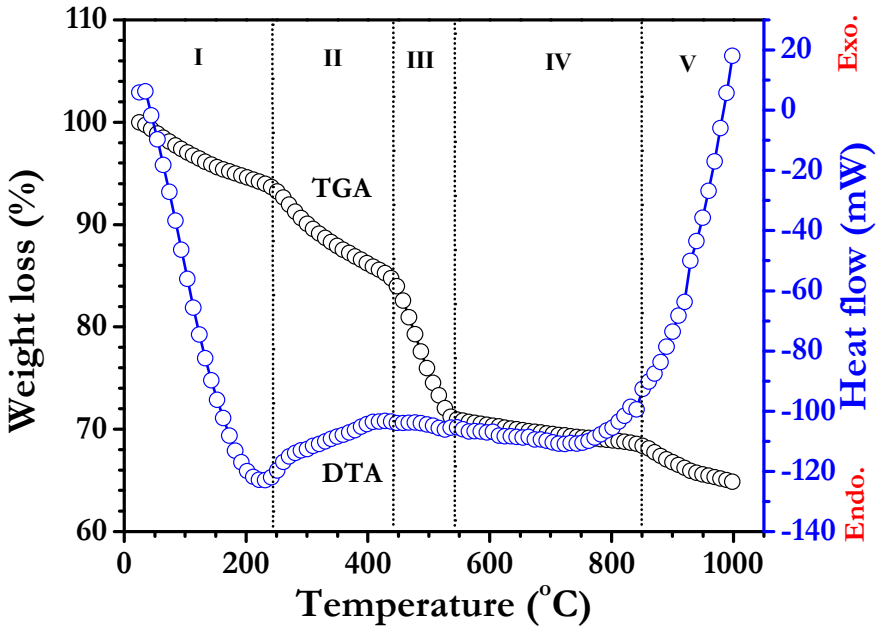

Figure S1 Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) (temperature range: 20-1000 °C heating rate at 5°C min^{-1}) for as synthesized Co_3S_4 NS. This TGA have five distinct stage of weight losses, the first weight loss stage ended at 240 °C, stemming from evaporationof trace water with organic content *i.e.* Thioacetamide and corresponding to the formation of CoS_2 phase, it's an endothermic reactions. The second weight loss began at 240- 440 °C was attributed to the de-sulfurization of CoS_2 phase in the exothermic backbone and formation of Co_3S_4 phase. Following this, desulfurization were caused by formation of different crystalline CoS (440 – 550 °C) and Co_9S_8 (550 – 840 °C) phases occurred at different temperatures within from 450 to 1000 °C.

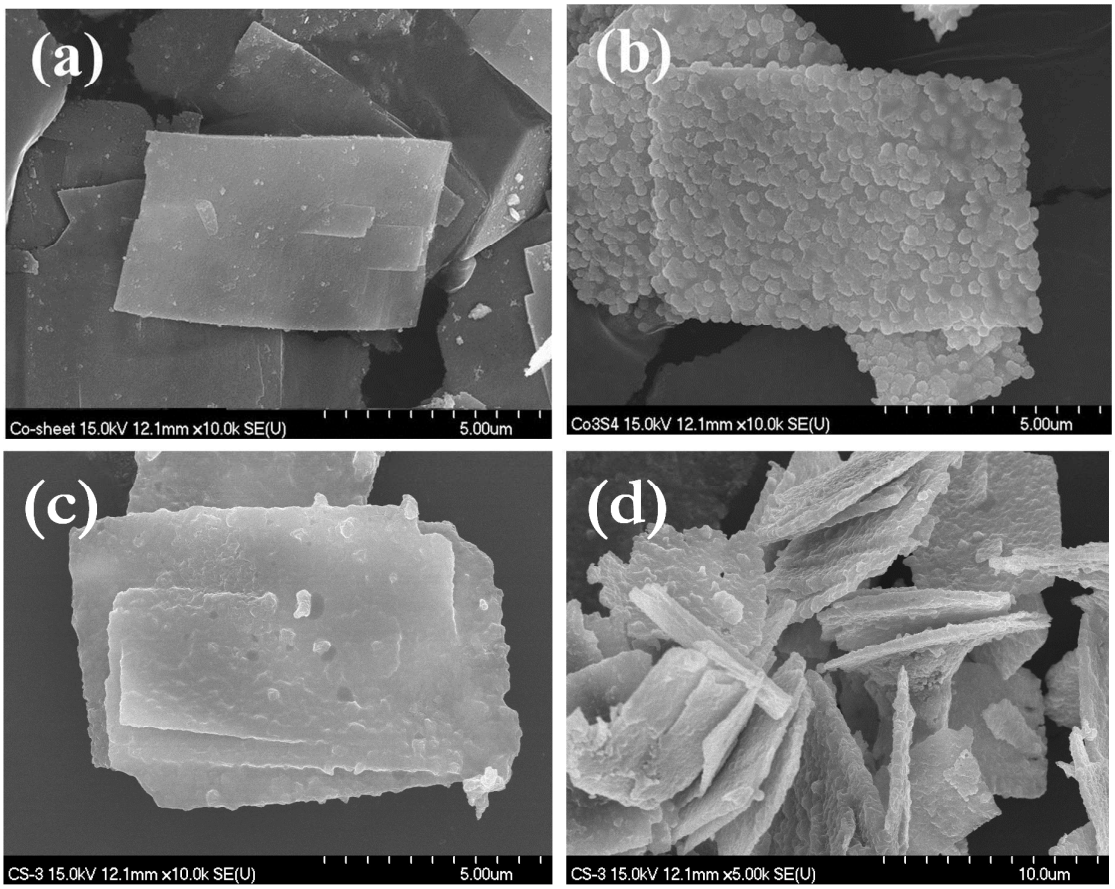

Figure S2 FE-SEM images for (a) Pristine Co_3O_4-NS, (b) Co_3S_4-NS at 400 ºC, (c) Co_3S_4-NS at 300 ºC for higher magnification, and (d) Co_3S_4-NS at 300 ºC for lower magnification.

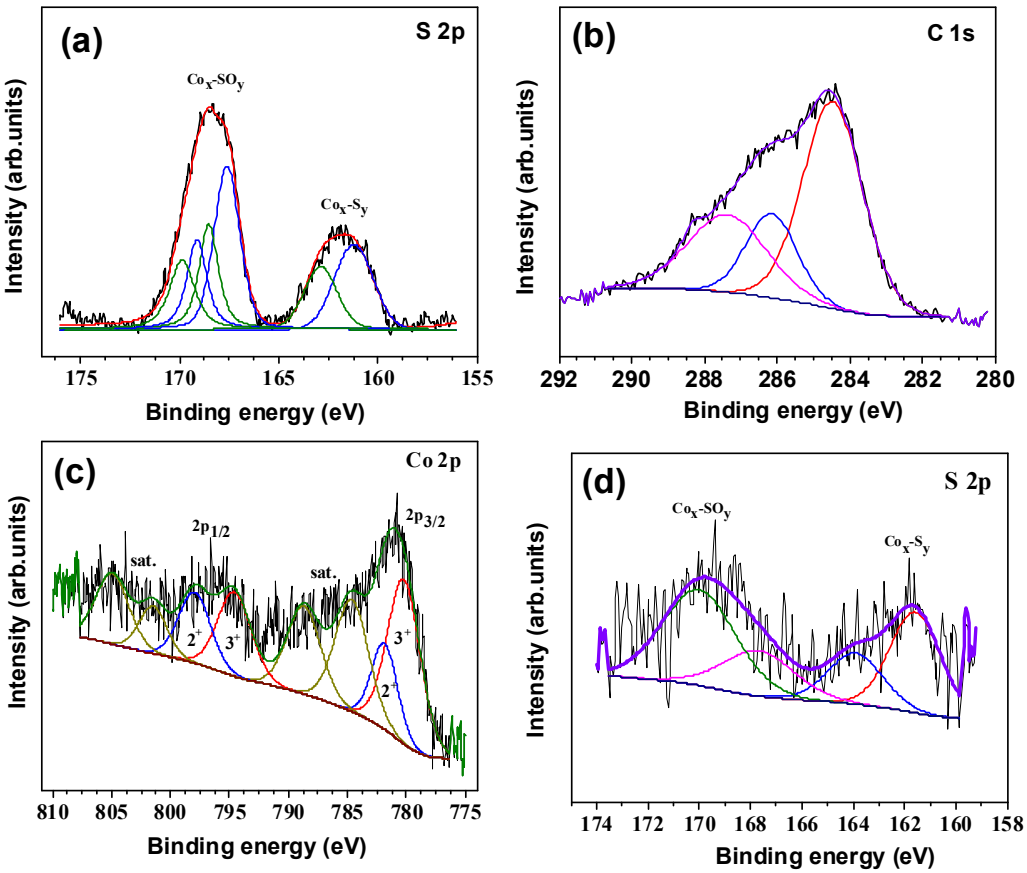

Figure S3 XPS spectra of CS-4 NS (a) S2p and (b) C1s peaks XPS spectrum of cycled electrode (c) Co 2p and (d) S 2p peaks

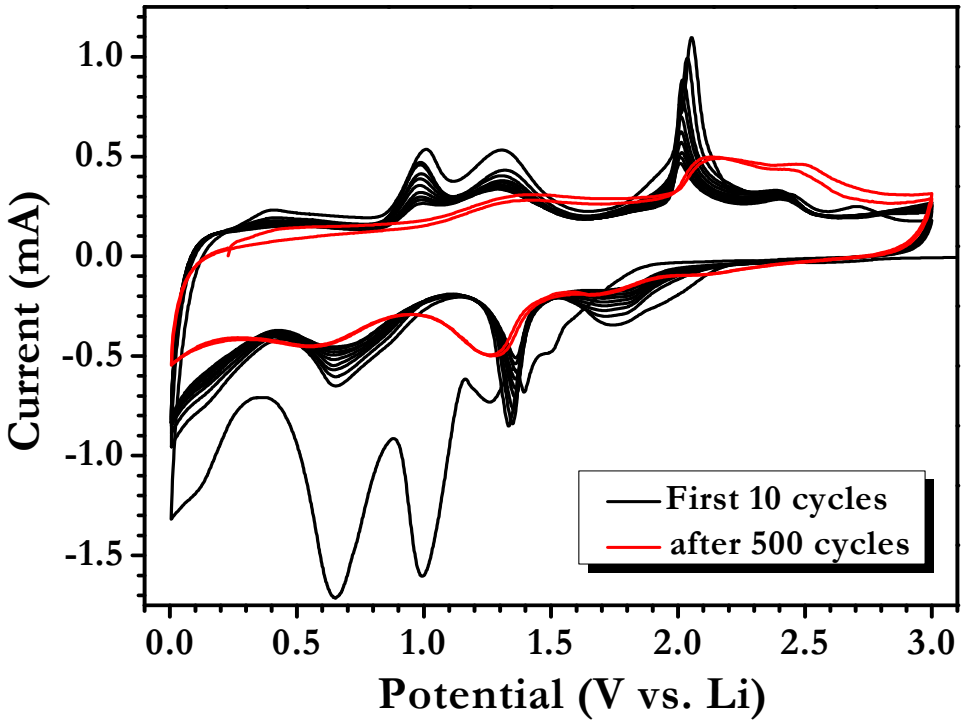

Figure S4 Comparative redox patterns of the pristine and after 500 cycles charge-discharge CS-4 NS electrode cyclic voltammogram collected at slow scan rate of 0.1 mV s^{-1} between 0.01 to 3V *vs.* Li at room temperature.