Supporting Information

Hybrid composite $Ni(OH)_2@NiCo_2O_4$ grown on carbon fiber paper for high-performance supercapacitors

*Liang Huang[12], Dongchang Chen[2], Yong Ding[2], Zhong Lin Wang[2], Zhengzhi Zeng[1] and Meilin Liu[2]**

[1] Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

[2]School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, Georgia 30332-0245, United States

Experimental detail:

All the reagents used in the experiment were of analytical grade and used without further purification. Commercial carbon fiber papers (from Fuel Cell Store) were cleaned in 0.1M H2SO4 solution prior to deposition.

Preparation of $Ni(OH)_2/NiCo_2O_4$ and $Ni(OH)_2/Co_3O_4$ arrays on the carbon fiber paper (CFP).

First, self-supported $NiCo_2O_4$ nanosheet arrays on the CFP were prepared by a facile eletrodeposition followed a calcinations progress. The electrodeposition was performed in a standard three-electrode glass cell at 25 °C, CFP as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter-electrode. The electrolyte for electrodeposition of $Co_{2x}Ni_x(OH)_2$ was70 ml of 0.1M metal ion solution, with the Ni^{2+}/ Co^{2+} concentration ratios of 1:2. The $Co_xNi_{1-x}(OH)_2$ nanosheets were deposited by the potential static with -1.0 V for 10 mins. The substrates were taken off and rinsed with DI water and ethanol with the assistance of ultrasonication, and dried in air. Then, the substrate calcined in the furnace at 300°C for 2h to convert to $NiCo_2O_4$ sheets. The mass loading of $NiCo_2O_4$ sheets for electrodeposition of 10 minutes is 0.6 mg/cm^2. The mass density of CFP is 10mg/cm^2.

Then, the self-supported $NiCo_2O_4$ nanosheet arrays were used as the scaffold for $Ni(OH)_2$ growth through another cathodic electrodeposition using the same experimental arrangement except that the working electrode was changed to self-supported $NiCo_2O_4$ nanosheet arrays and the electrolyte to 70 ml of 0.1M Ni^{2+} solution. After the deposition,

the samples were rinsed with DI water and ethanol several times, and dried in air. For electrodeposition of 10minutes, the mass loading of $Ni(OH)_2$ is 1mg/cm^2.

The procedures for fabrication of $Ni(OH)_2/Co_3O_4$ arrays on the CFP is the same as that for synthesis of $Ni(OH)_2/NiCo_2O_4$ on CFP, except that the electrolyte in the first step was changed to 0.1M Co^{2+} solution to get Co_3O_4 sheets on the CFP. The mass loading of Co_3O_4 and $Ni(OH)_2$ on the CFP are 0.7 and 1.1mg/cm^2 , respectively, after electrodeposition of 10 minutes.

The phases of the samples were examined by X-ray diffraction (XRD) analysis (PW-1800 system). The microstructure and morphology were examined using a scanning electron microscope (LEO 1530 field emission SEM) and a high resolution transmission electron microscope (JEOL 4000 EX).

Electrochemical Measurement

Cyclic voltammetry (CV) and galvanostatic charge-discharge cycling were performed using a classical three-electrode configuration. The cyclic voltammograms were acquired in a potential range between 0 and 0.6 V at different scan rates, and the charge/discharge processes were performed by cycling the potential from 0 to 0.45 V at different current densities in 1 M KOH aqueous electrolyte. These standard electrochemical experiments were performed using a Solartron 1286 electrochemical interface and a Solartron 1255 HF frequency response analyzer. The cyclic stability was evaluated by cyclic voltammetry measurements at a current density of 5 mA/cm^2 for over 1 000 cycles, using an Arbin testing system (MSTAT).

Areal capacitance and specific capacitance were calculated from the galvanostatic charge and discharge curves, using the following equations :

$$AC = \frac{J\,t}{\Delta V} \quad (1)$$

$$SC = \frac{J\,t}{m\Delta V} \quad (2)$$

where J is charge or discharge current, t is the time for a full discharge, m indicates the mass of the active material, and ΔV represents the voltage change after a full charge or discharge.

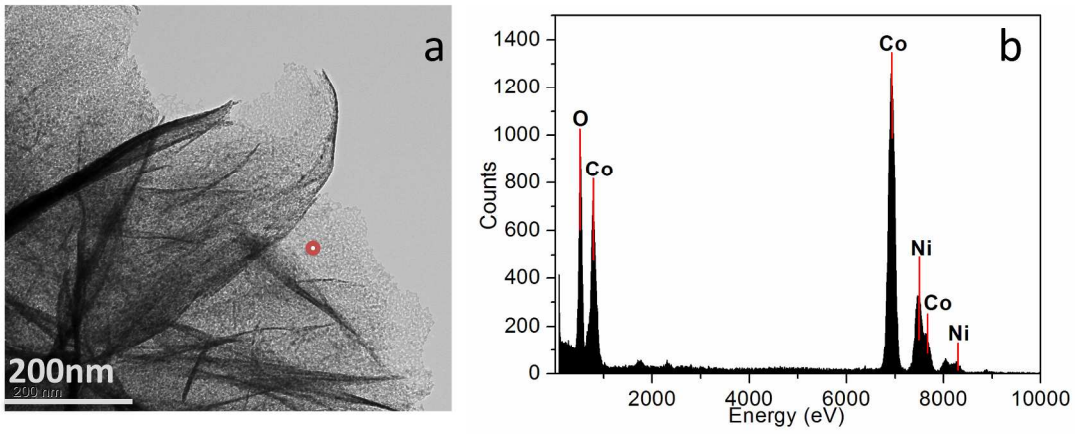

Figure S1. TEM image of $NiCo_2O_4$ and its EDS spectrum. (the red oring marks the area of EDS analysis)

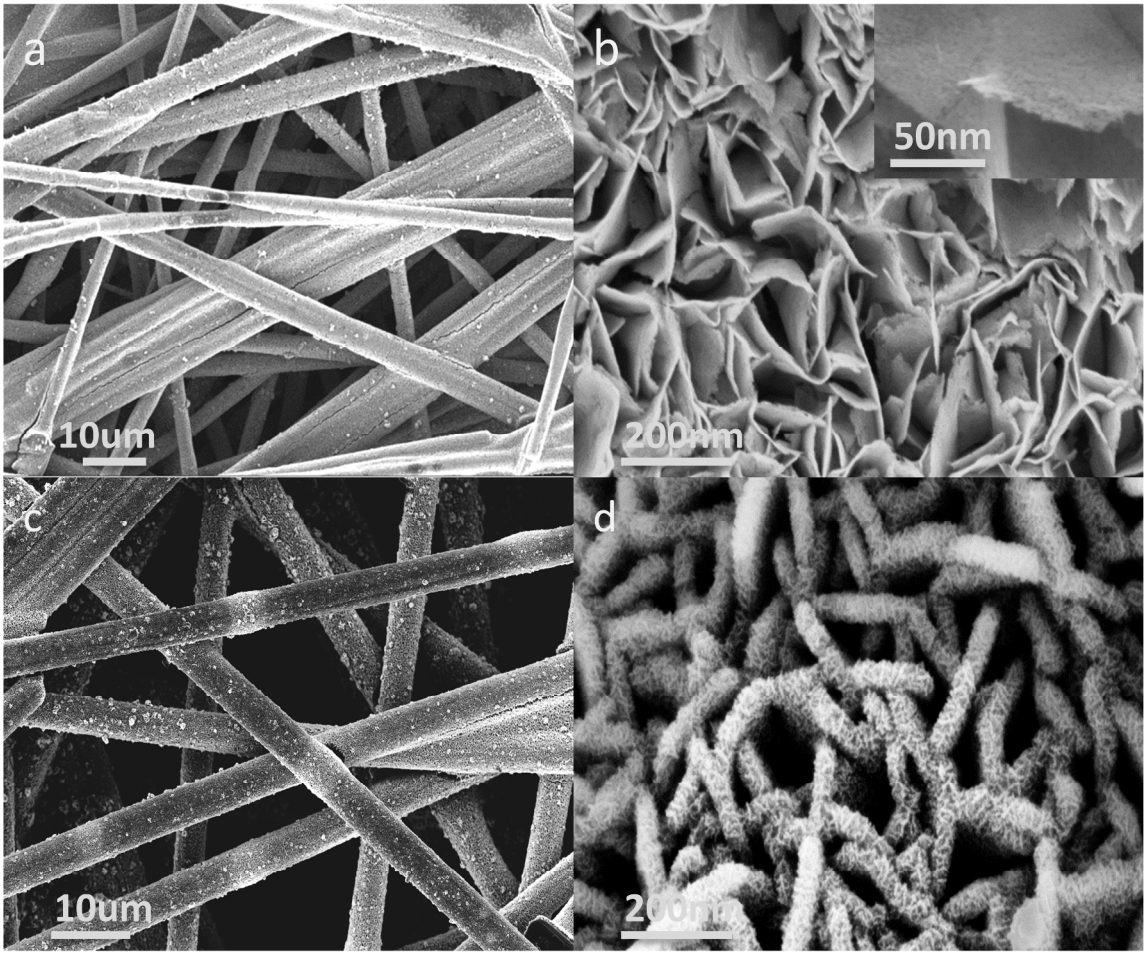

Figure S2. (a, b) SEM images of Co_3O_4 sheets on CFP; (c, d) SEM images of $Ni(OH)_2/Co_3O_4$ hybrid arrays on CFP.

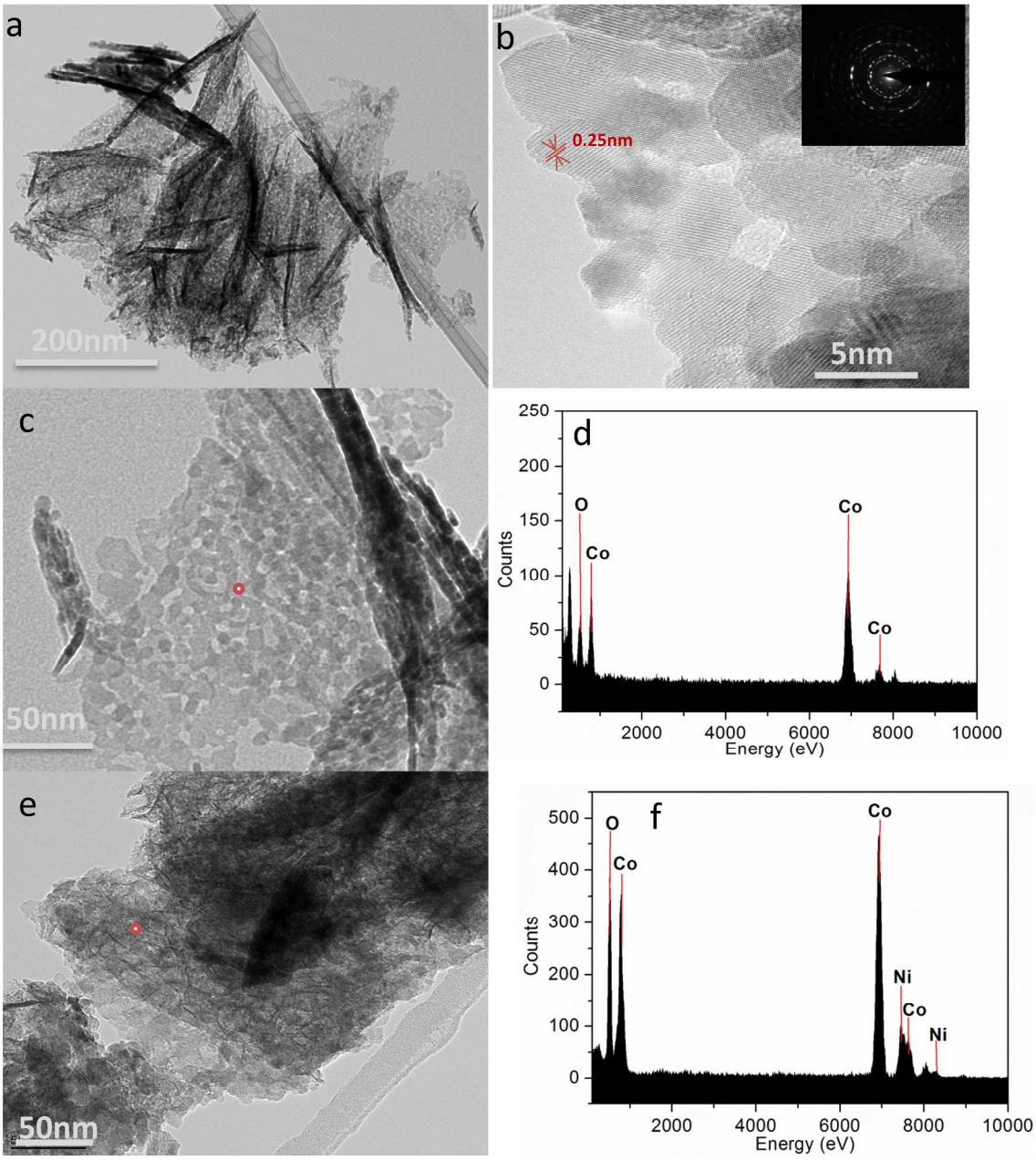

Figure S3. (a, c, d) TEM images of Co_3O_4 sheets on the CFP and an EDS spectrum ; (b)HRTEM image of Co_3O_4 sheets (the inter is an SEDP). (e,f) TEM image of $Ni(OH)_2/Co_3O_4$ hybrid arrays and an EDS spectrum. (the red oring marks the area of EDS analysis)

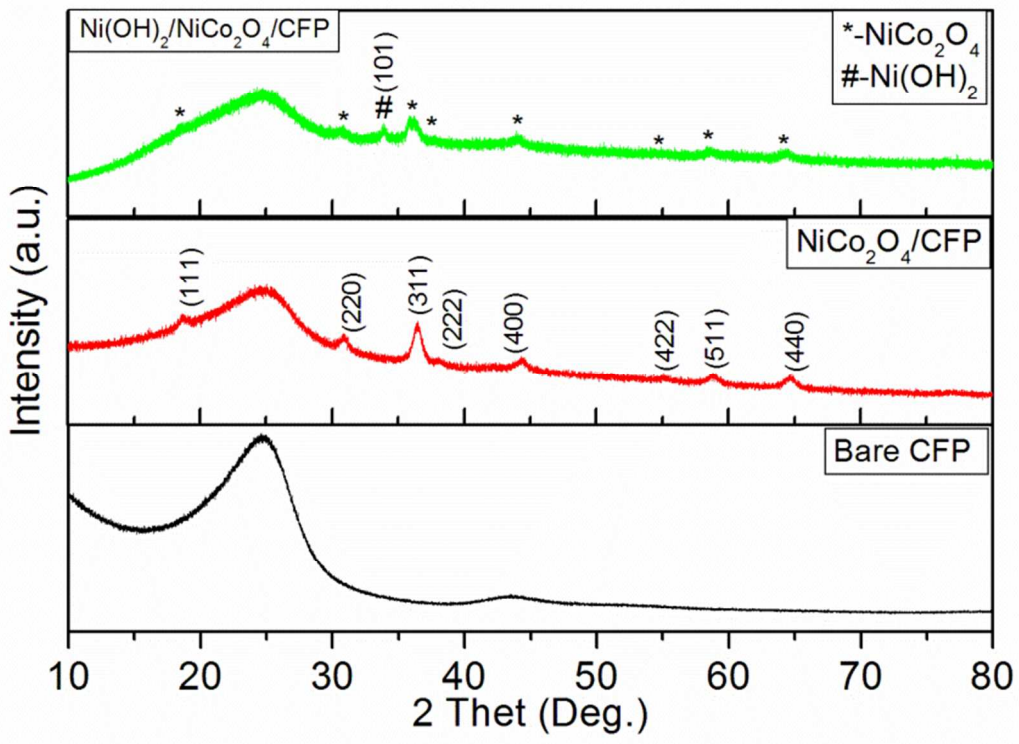

Figure S4: Crystal phases of the CFP supported $NiCo_2O_4$ sheets and $Ni(OH)_2$/ $NiCo_2O_4$/ CFP hybrid arrays.

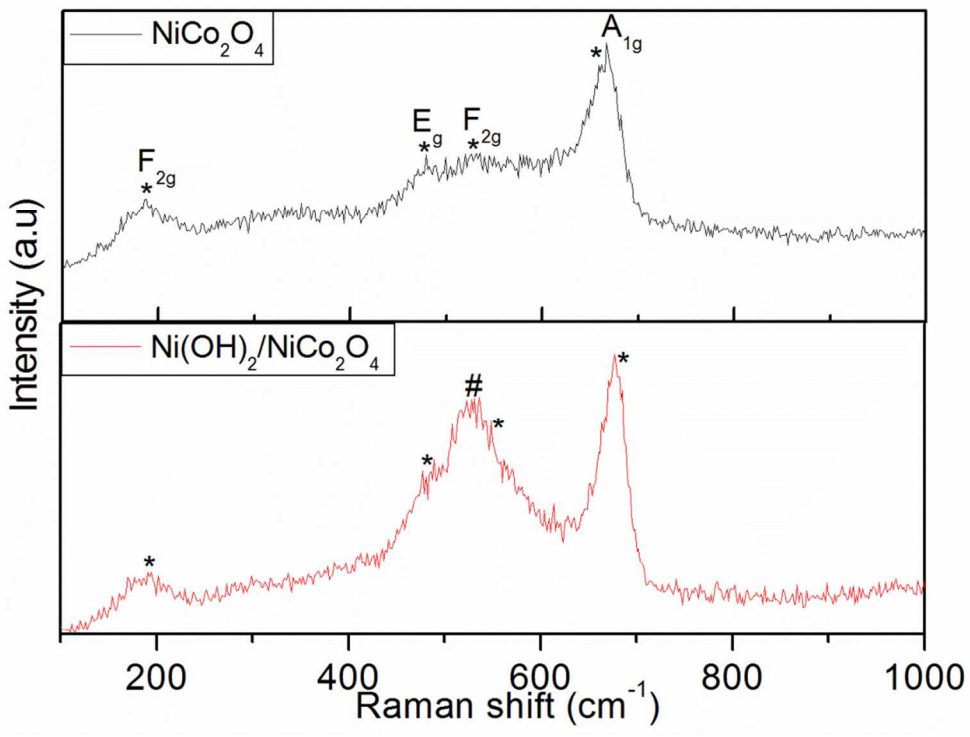

Figure S5: Raman spectra of $NiCo_2O_4$ nanosheets and $Ni(OH)_2$ /$NiCo_2O_4$.

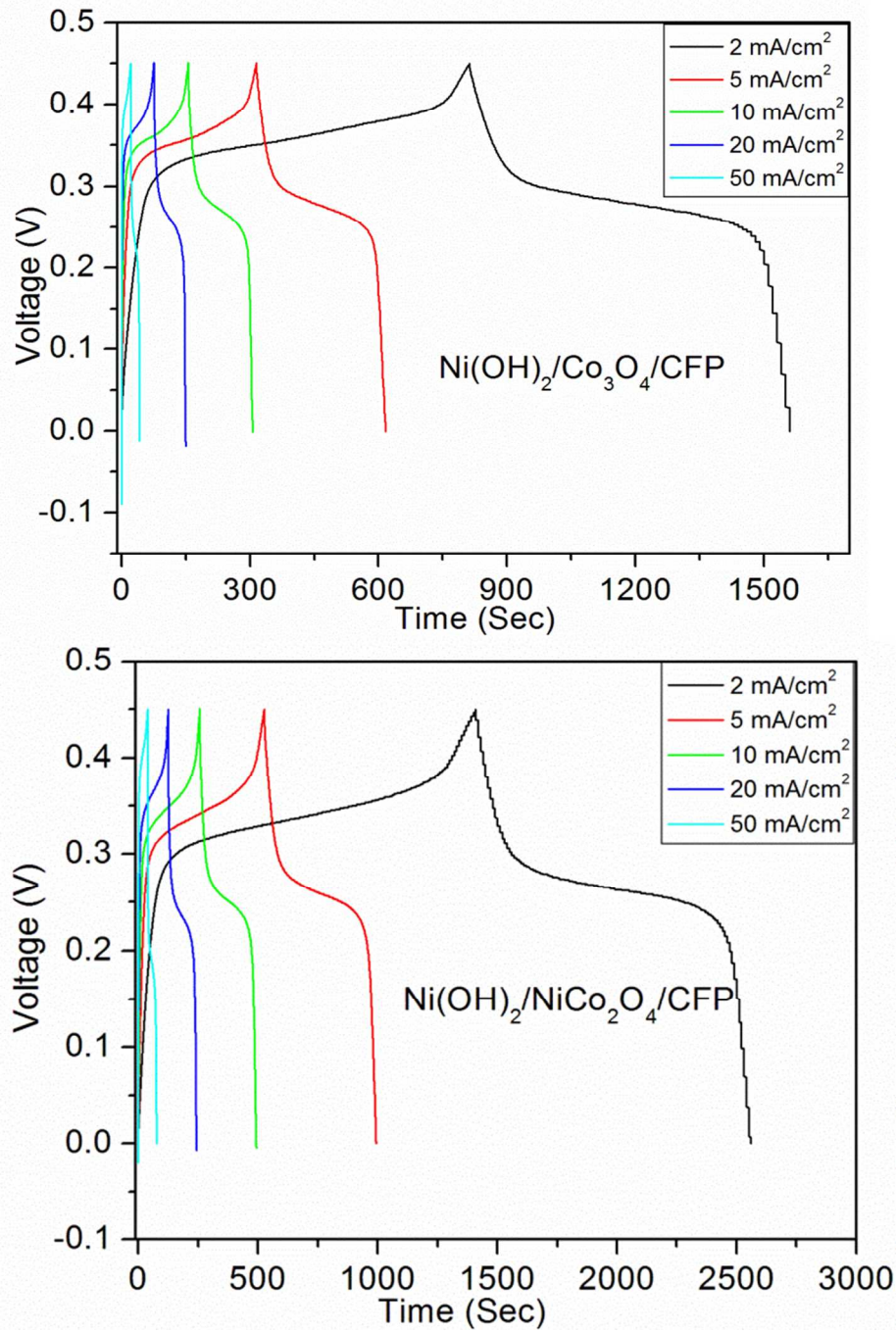

Figure S6. Galvanostatic charge and discharge curves of $Ni(OH)_2$/ $Co3O_4$/ CFP and $Ni(OH)_2$/ $NiCo_2O_4$/ CFP hybrid composite at different current densities.

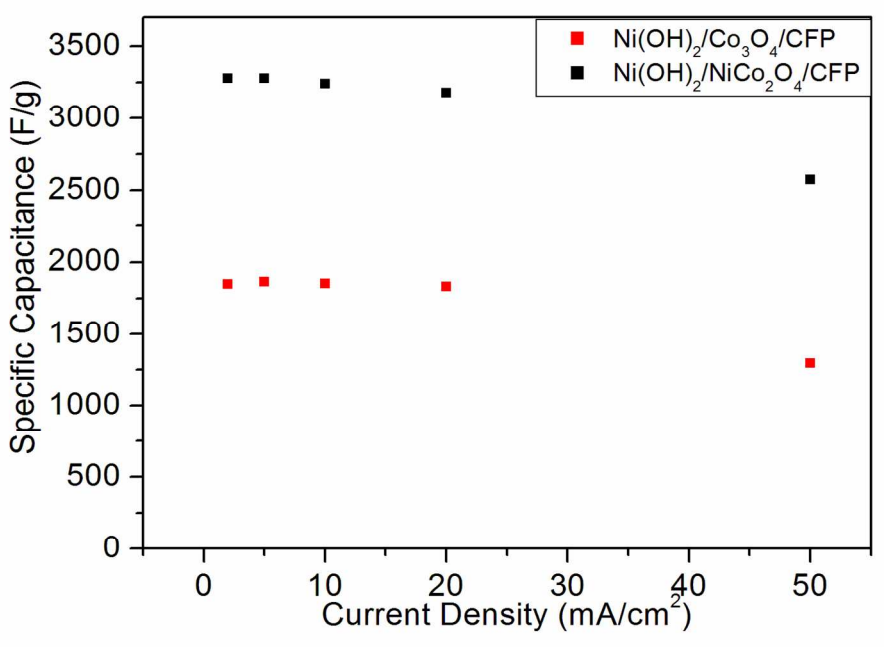

Figure S7. Specific capacitance of $Ni(OH)_2$/ $Co3O_4$ and $Ni(OH)_2$/ $NiCo_2O_4$ on the CFP. (Base on mass of metal oxide and hydroxide)

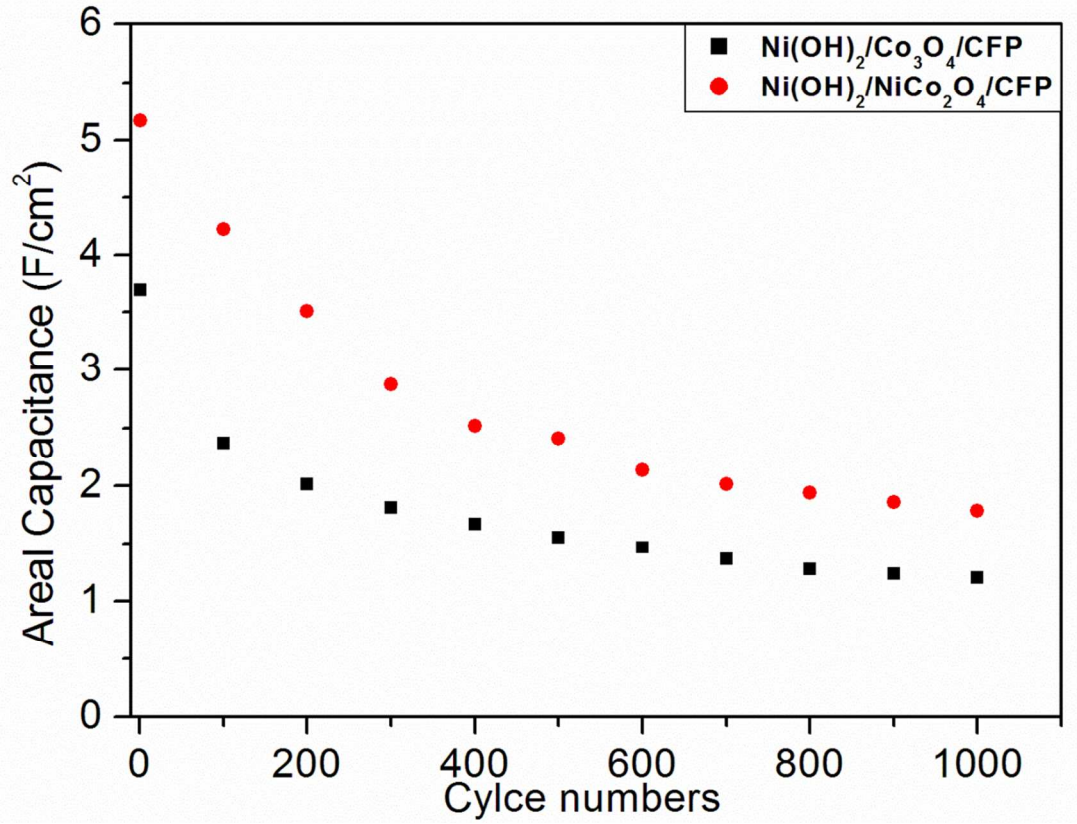

Figure S8. Areal capacitance of hybrid composite electrodes under current density of 5 mA/ cm^2 for cycling 1000 times.

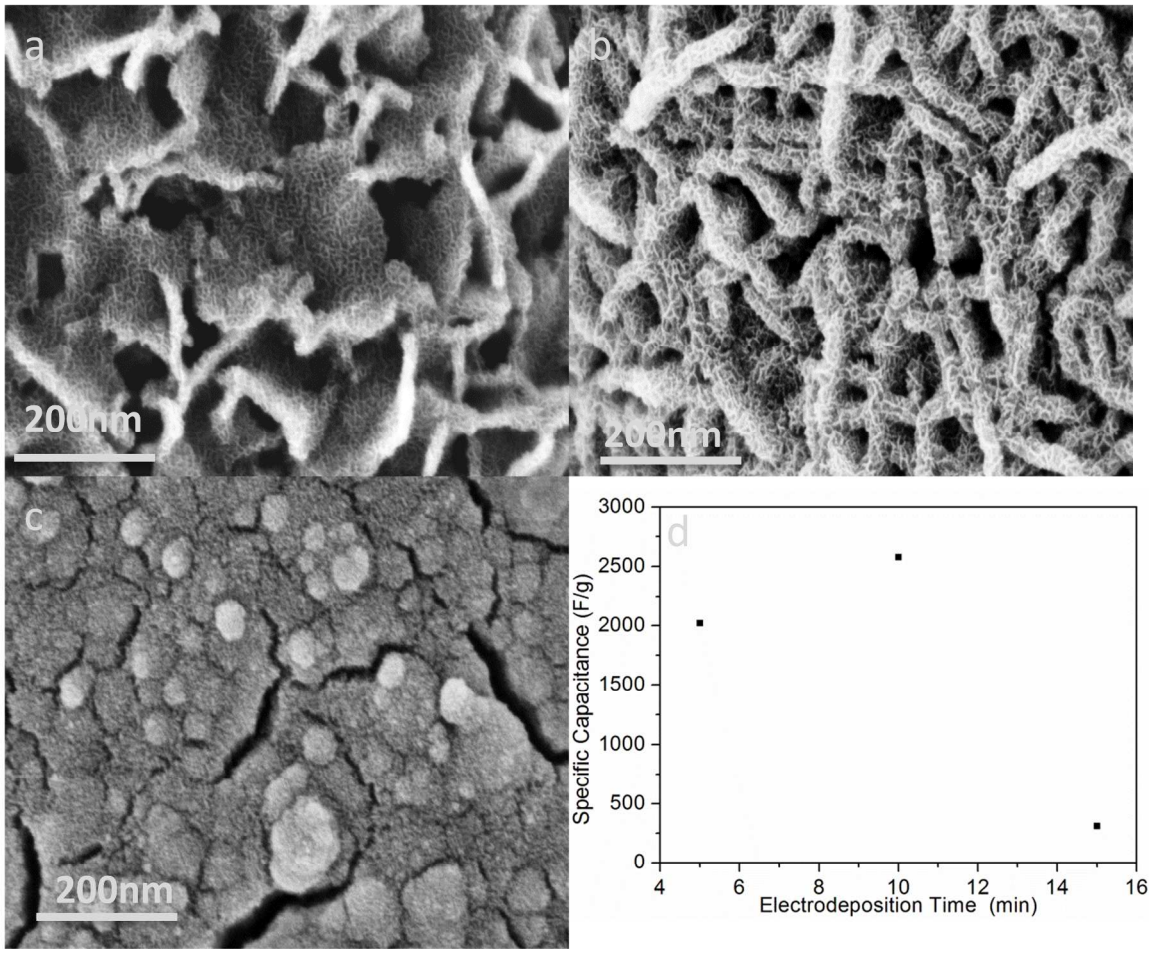

Figure S9. SEM image of $Ni(OH)_2$/ $NiCo_2O_4$ hybrid arrays on the CFP at different $Ni(OH)_2$ electrodeposition time:(a)5 mins; (b)10 mins; (c)15 mins. (d) Specific capacitance of $Ni(OH)_2$/ $NiCo_2O_4$ based on different $Ni(OH)_2$ electrodeposition time at the current density of 50mA/cm^2.

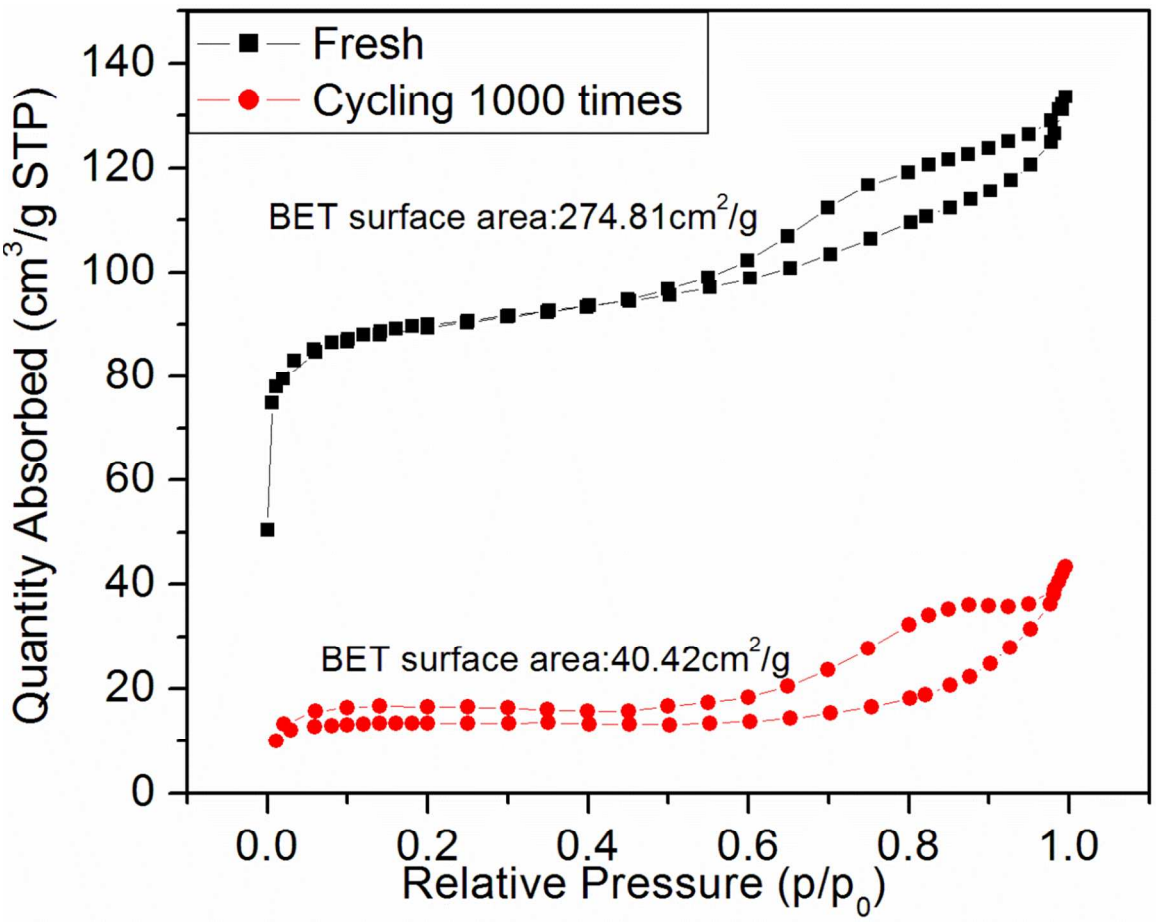

Figure S10 BET of $Ni(OH)_2$/ $NiCo_2O_4$/CFP before and after 1 000 cycles at a current density of 5 mA/cm^2 in the potential range of 0-0.45V.