Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Integration of Nickel-Cobalt Double Hydroxide Nanosheets and Polypyrrole Film with Functionalized Partial-Exfoliated Graphite for Asymmetric Supercapacitor with Improved Rate Capability

Yu Song, Xiang Cai, Xinxin Xu*, Xiao-Xia Liu*

Department of Chemistry, Northeastern University, Shenyang, 110819, China

Corresponding authors: Xiao-Xia Liu, Xin-Xin Xu.

Fax: +86 024 83684323; Tel: +86 024 83684323;

E-mail: xxliu@mail.neu.edu.cn; xuxx@mail.neu.edu.cn

1. Calculations

1.1 Specific capacitance calculation based on constant current charge/discharge experiments

Gravimetric and areal capacitance of a single electrode from the constant current charge-discharge profile are calculated from equation S1 and S2:

$$C_m = \frac{It}{m\Delta U} \qquad \text{(Equation S1)}$$

$$C_a = \frac{It}{S\Delta U} \qquad \text{(Equation S2)}$$

Where C_m and C_a are the gravimetric and areal specific capacitance (F/g or mF/cm^2), S is the electrode area (cm^2), I represents the discharge current (mA), m is the mass loading of the oxides or polymer (mg), t is the discharge time (s) and ΔU is the potential window (V).

Nearly the whole surfaces of FEG are covered by Ni-Co DH or PPy in the hybrid electrodes (Figures 2a, 3b and 3h-i), thus its contact with electrolyte is blocked and so could rarely take part in the charge storage process. The capacitive contribution of FEG substrate in the hybrid electrodes is negligible as charges is mainly stored at the surface or near surface of the hyrbid materials through faradic reactions.[S1-S2]

Gravimetric capacitance of the ASC device from the constant current charge-discharge profile is calculated from equation S3:

$$C = \frac{It}{mU} \qquad \text{(Equation S3)}$$

Where C is the specific capacitance of the ASC (F/g), I represents the discharge current (mA), m is the mass loading of the active materials in the two electrodes (mg), t is the discharge time (s) and U is the potential window of the ASC (V).

1.2 Energy density and power density calculations for the ASC device

Energy density (E, Wh/kg) and power density (P, kW/kg) are calculated using the following two equations:

$$E = \frac{1000}{2\times 3600} C\,U^2 \qquad \text{(Equation S4)}$$

$$P = \frac{3600\times E}{1000\times t} \qquad \text{(Equation S5)}$$

Where C is the specific capacitance (F/g), U is the operating voltage (V) and t is the discharge time (s) measured in constant current charge/discharge experiments.

1.3 Charge balance in ASCs

To maximize performance of pseudocapacitor device, charges stored in anode and cathode should be balanced by $Q_- = Q_+$. The charge stored in each electrode depends on their specific capacitance (C_m), their charge storage potential window (ΔU) and loading of the active materials on the electrode (m), according to equation S6:

$$Q = C_m \times \Delta U \times m \qquad \text{(Equation S6)}$$

In order to get $Q_- = Q_+$, the mass balancing should follow equation S6:

$$\frac{m_-}{m_+} = \frac{(C_+)\times(\Delta U_+)}{(C_-)\times(\Delta U_-)} = \frac{2442\times 0.5}{560\times 0.8} = 2.73$$

However, the PPy in anode is less stable than the Ni-Co DH in cathode, therefore less charges can be stored in the anode compared to that stored in the cathode after several charge/discharge cycles of the ASC operation. Serious decay of PPy's electroactivity will be finally directed due to the enlargement of its charge storage potential window for charge balance. To improve the stability of the device, ASCs with different ratios of the loading of electroactive materials in anode and cathode were assembled to adjust the ratio of the charges can be stored in anode and cathode ($R = Q_-/Q_+ = 1.0$, 1.2, and 1.3):

FEG/PPy//FEG/Ni-Co DH-1.0, $R = Q_-/Q_+ = 1.0$

$$\frac{m_-}{m_+} = \frac{(C_+)\times(\Delta U_+)}{(C_-)\times(\Delta U_-)} = \frac{2442\times 0.5}{560\times 0.8} = 2.73$$

FEG/PPy//FEG/Ni-Co DH-1.2, R = Q_-/Q_+ = 1.2

$$\frac{m_-}{m_+} = \frac{1.2\times(C_+)\times(\Delta U_+)}{(C_-)\times(\Delta U_-)} = \frac{1.2\times 2442\times 0.5}{560\times 0.8} = 3.27$$

FEG/PPy//FEG/Ni-Co DH-1.3, R = Q_-/Q_+ = 1.3

$$\frac{m_-}{m_+} = \frac{1.3\times(C_+)\times(\Delta U_+)}{(C_-)\times(\Delta U_-)} = \frac{1.3\times 2442\times 0.5}{560\times 0.8} = 3.55$$

2. Supplementary Figures

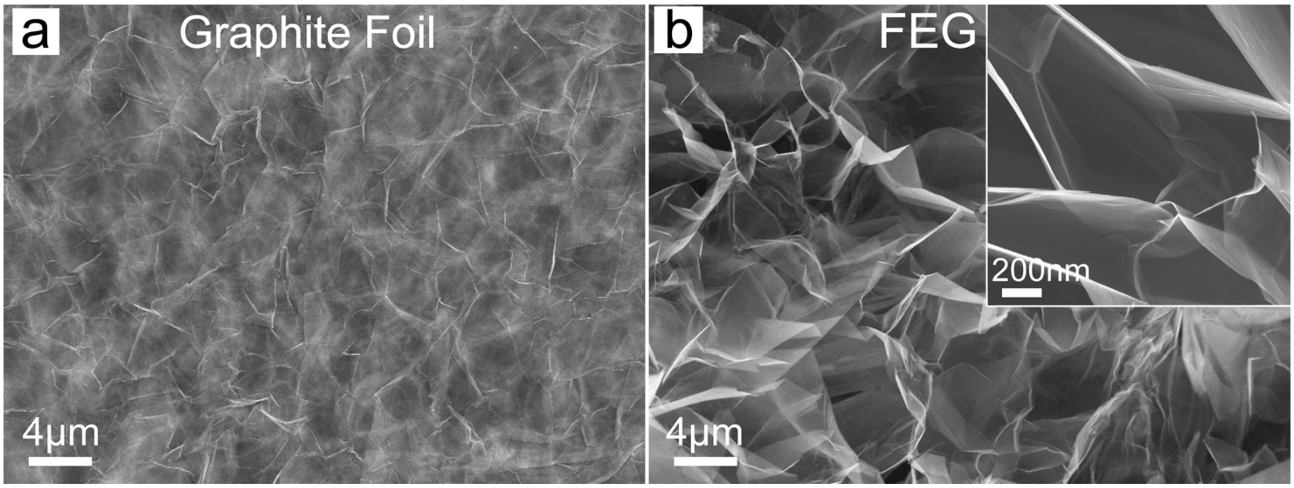

Figure S1 SEM image of (a) untreated graphite foil and (b) FEG. Inset shows the magnified image of FEG.

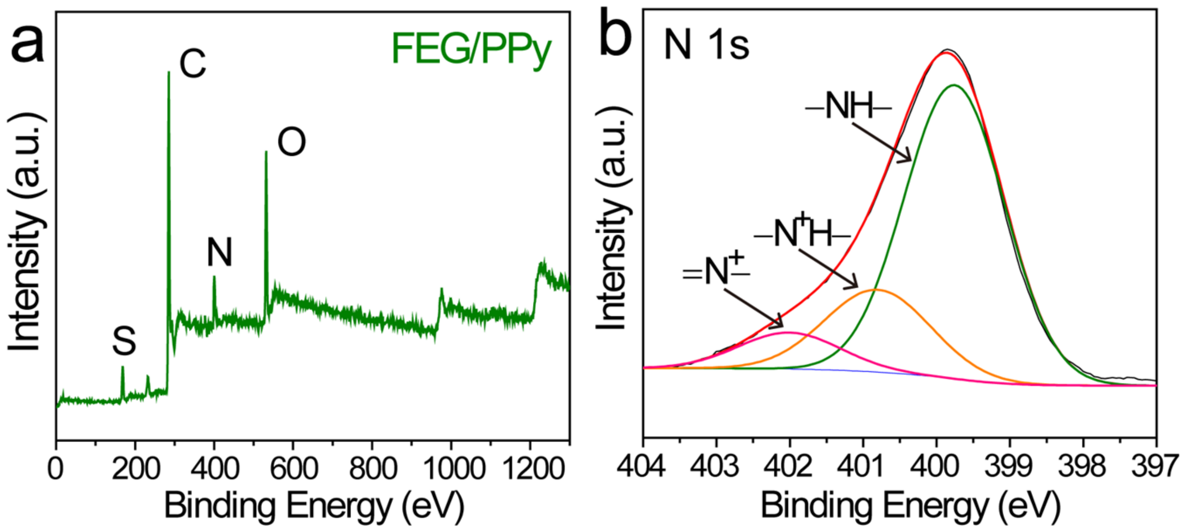

Figure S2 XPS survey spectrum of FEG/PPy (a) and N 1s spectrum of FEG/PPy (b).

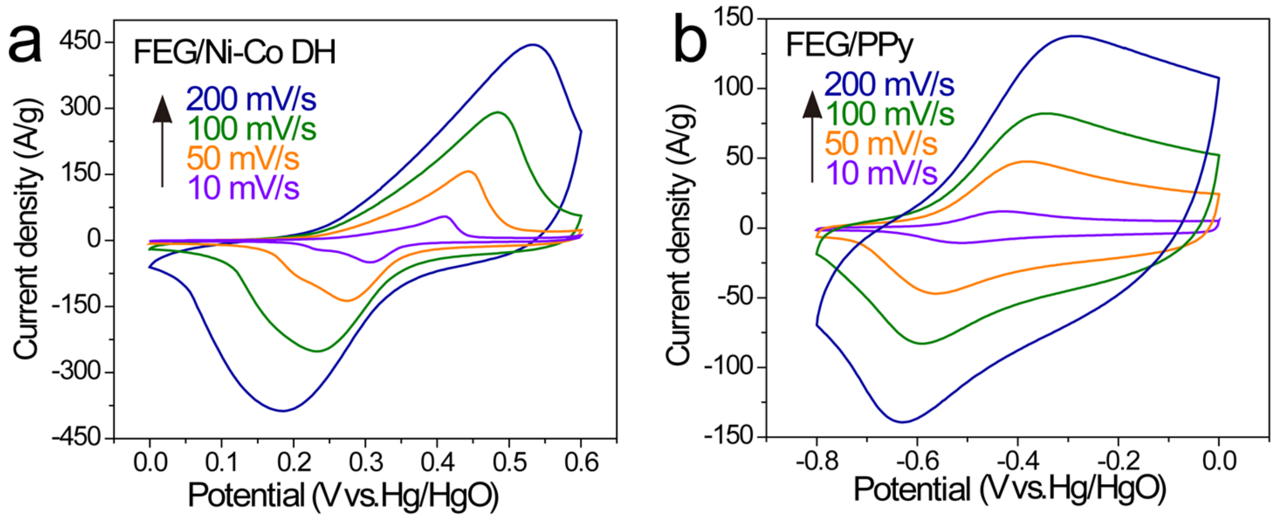

Figure S3 CV profiles of FEG/Ni-Co DH and FEG/PPy hybrid electrodes.

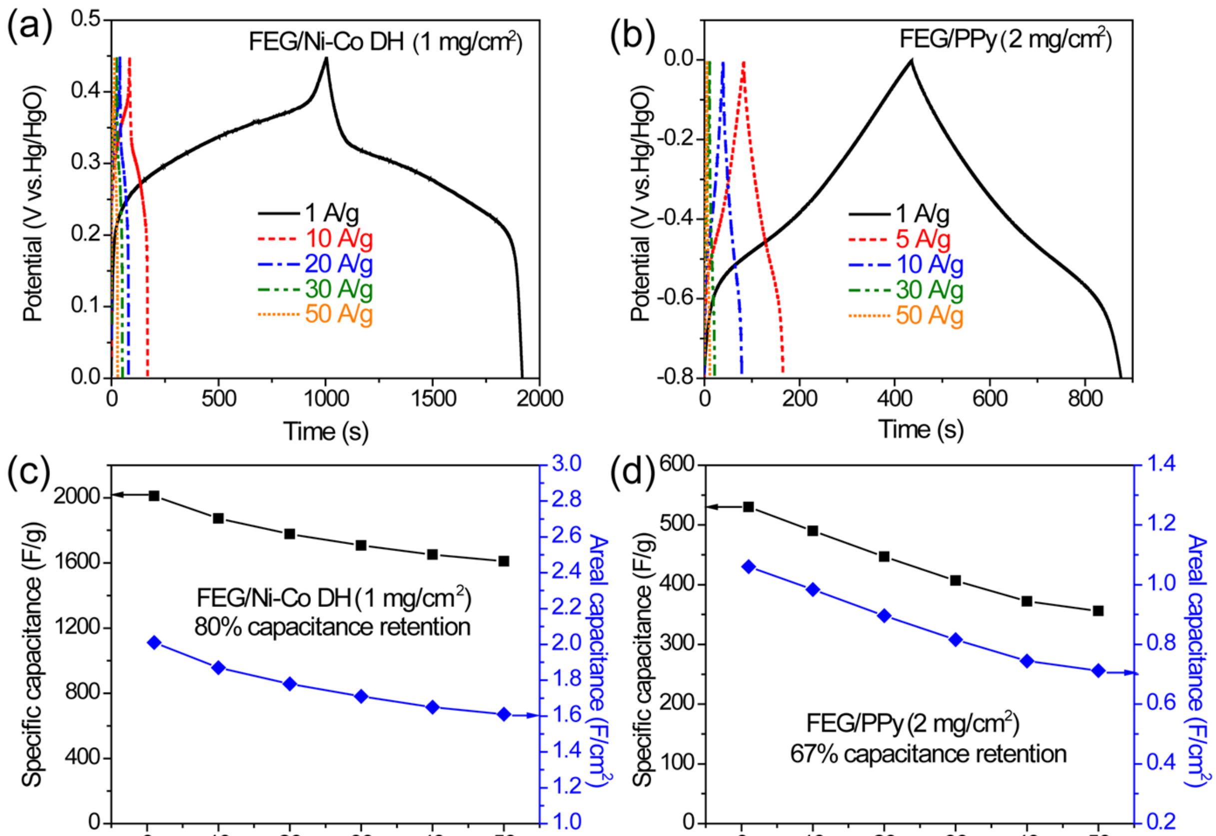

Figure S4 Constant current charge-discharge profiles of FEG/Ni-Co DH (mass loading: 1 mg/cm^2) and FEG/PPy (mass loading: 2 mg/cm^2) measured at different current densities (a, b). Gravimetric/areal specific capacitance of FEG/Ni-Co DH (mass loading: 1 mg/cm^2) and FEG/PPy (mass loading: 2 mg/cm^2) measured at different current densities (c, d).

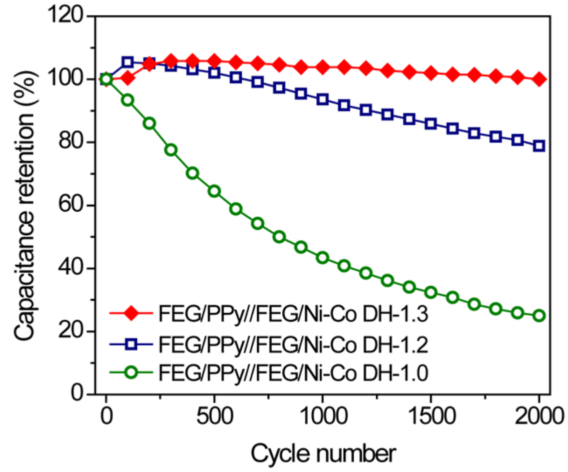

Figure S5 Cycling stability of the model ASCs with different R = Q_-/Q_+ (R=1, 1.2, and 1.3) after 2000 cycles.

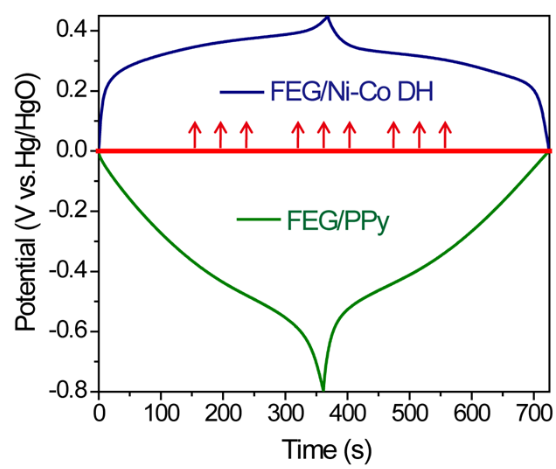

Figure S6 Schematic diagram of positively shifting upper potential limit of PPy for charge balance with cathode

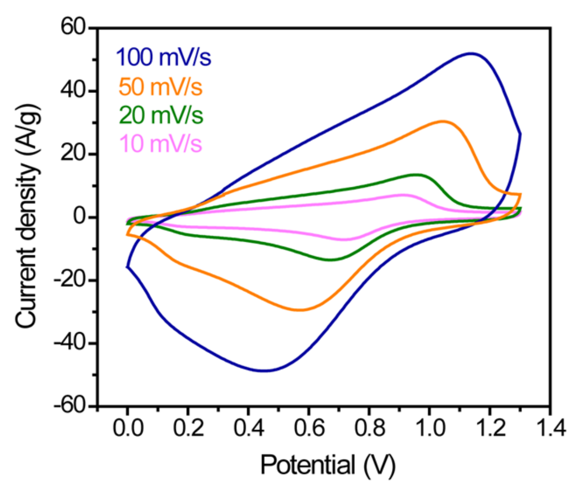

Figure S7 CV curves of FEG/PPy//FEG/Ni-Co DH-1.3 at different scan rates.

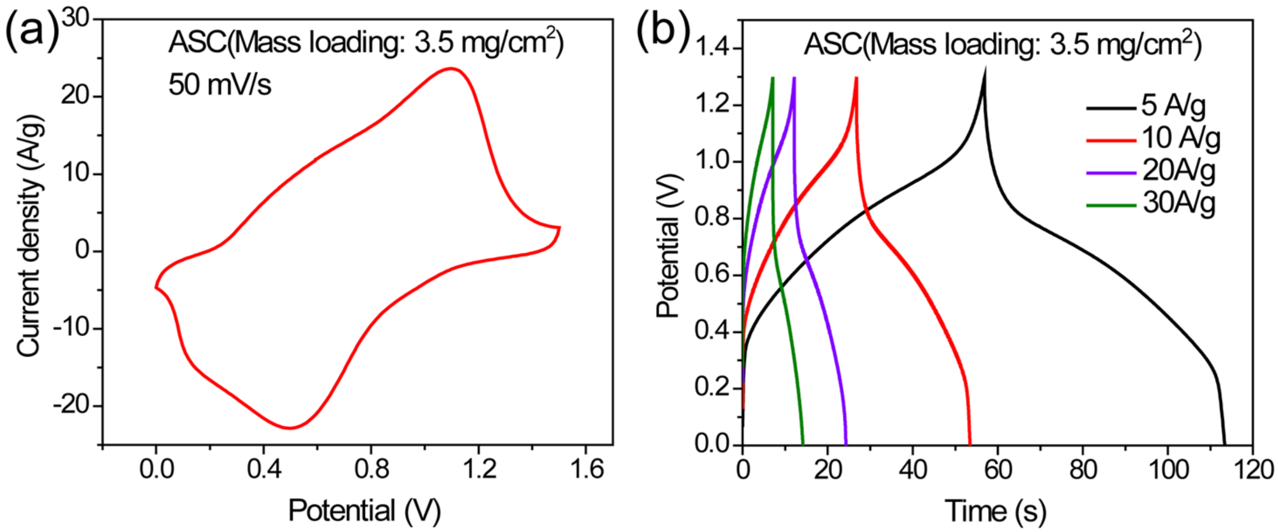

Figure S8 CV and constant current charge/discharge curves of ASC with higher active materials mass loading of 3.5 mg/cm^2.

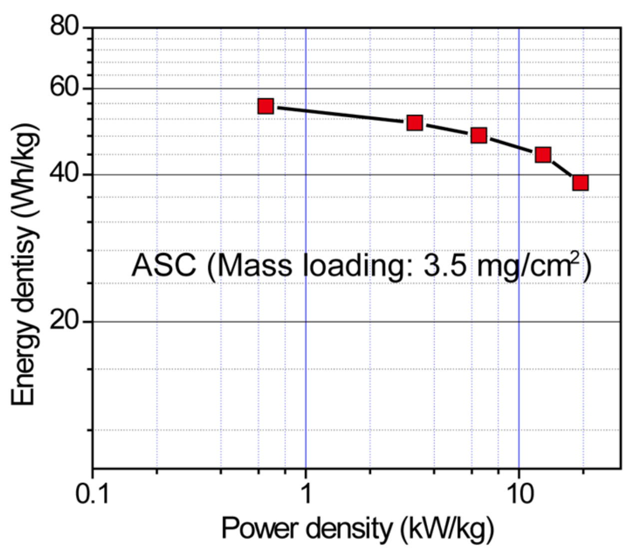

Figure S9 Ragone plots of ASC with higher active mass loading of 3.5 mg/cm^2.

In addition, even when the acitive mass loading of the ASC was increased to 3.5 mg/cm^2, a high energy density of 55.2 Wh/kg at power density of 0.65 W/kg and 38.5 Wh/kg at an ultra-high power density of 19.5 kW/kg could also be delivered.

Reference

[S1] J. Yan, E. Khoo, A. Sumboja, P. S. Lee, *ACS nano* **2010**, *4*, 4247-4255.
[S2] J. H. Kim, K. H. Lee, L. J. Overzet, G. S. Lee, *Nano lett.* **2011**, *11*, 2611-2617.