Supporting Information

Using Thiourea as a Catalytic Redox-active Additive to Enhance the Performance of Pseudocapacitive Supercapacitors

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1.Experimental Section

1.1 Preparation of PPH samples

PPH was synthesized according to the literature [1, 2]. Preparation of PVA with mass fraction of 10%: 1g PVA was dissolved in 9 mL distilled water, swelled at 60 °C and under magnetic stirring for 1 h, and then heated to 90 °C and stirred for 2 h to obtain PVA (10 wt%) solution. The prepared PVA solution (2 mL) and ABA (0.0364 g) were added into 835 mL HCl and 241 mL distilled water and 3.0 mmol AN, respectively to get solution A. 2 mmol of APS was added in distilled water (1 mL) to obtain solution B. The A and B solutions were respectively cooled at 0 °C in a mixture of ice and water, and then solution A was slowly transferred to solution B to form solution C under magnetic stirring. The resulting C solution was poured into the molder and stood for 24 h to synthesize PPH film, which was taken out and cleaned with deionized water to remove impurities.

1.2 Structure characterization

The thermal stability of samples was characterized by thermogravimetric analysis (TGA) on a ZCTA analyzer under a N_2 atmosphere from ambient temperature to 800 °C. The cystalline and phase purity of the composites were tested on Bruker D8 using Cu-Ka radiation in the 2θ range of 10° to 90°. Field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to analyze the morphology of samples. N_2 adsorption experiments were performed on an ASAP 2020 Plus instrument. The surface elements and valence states of the composites were analyzed by X-ray photoelectron spectroscopy (XPS) on VG instrument using X-ray source. Raman spectroscopic analysis was performed by a Renishaw micro Raman spectrometer under the irradiation of a 532 nm.

2.Supplementary figures

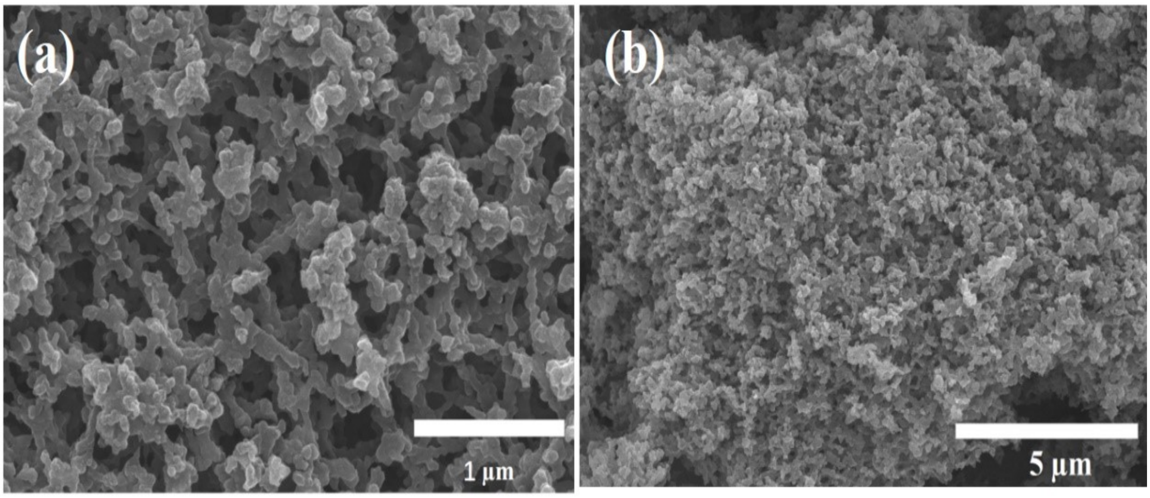

Fig.S1. PPH-600 SEM image.

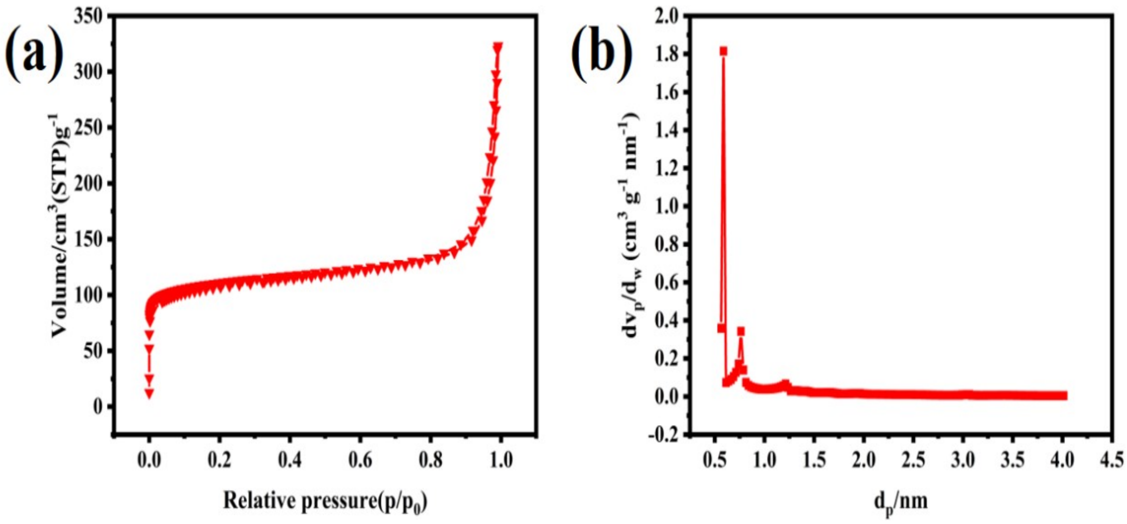

Fig.S2. N_2 adsorption-desorption isotherms and pore size of PPH-600.

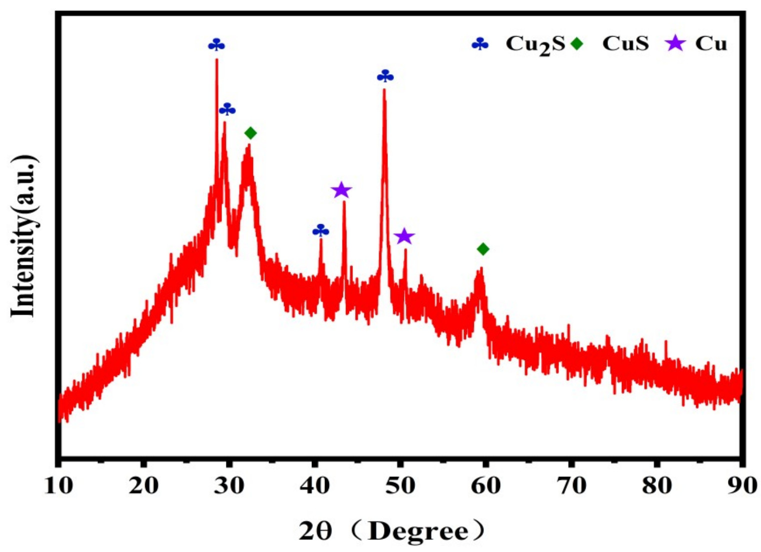

Fig.S3.XRD analysis of Cu@N-C-600 after 1000 CV cycles in KOH +KCl+ thiourea.

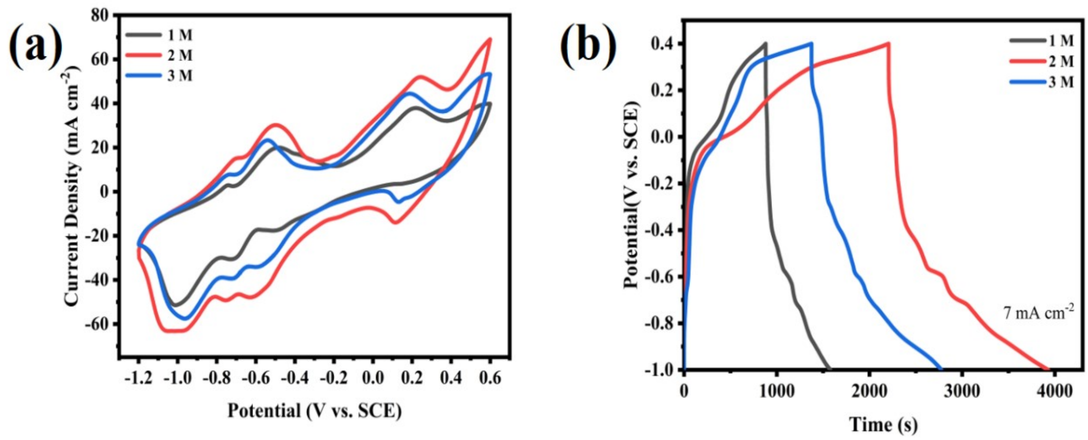

Fig.S4. Electrochemical test of Cu@N-C-600 samples prepared with different $CuCl_2$ concentrations (1-3 M). (a)CV at scan rate of 20 mV s^{-1} and (b) GCD curves at current density of 7 mA cm^{-2}.

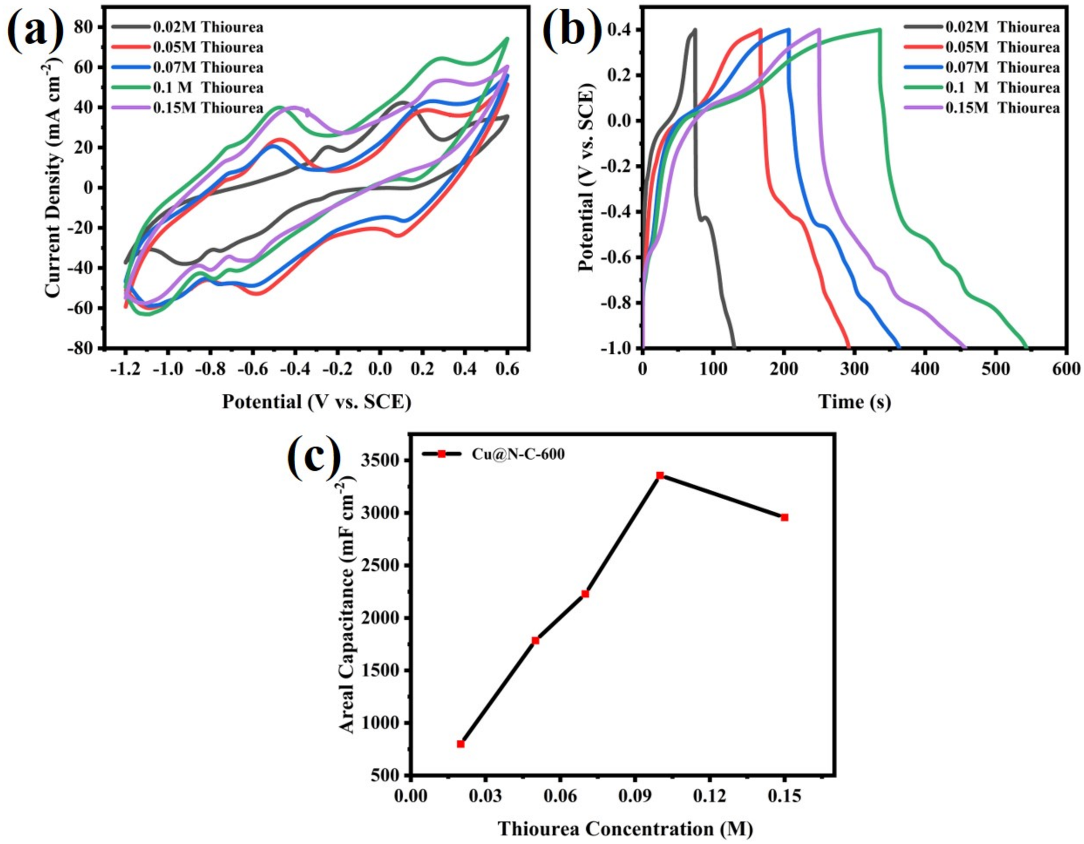

Fig.S5. Electrochemical properties of Cu@N-C-600 with different concentrations of thiourea in the electrolyte. (a)CV curves at scan rate of 20 mV cm^{-2}; (b)GCD curves at current density of 20 mA cm^{-2};(c) Areal capacitance of Cu@N-C-600.

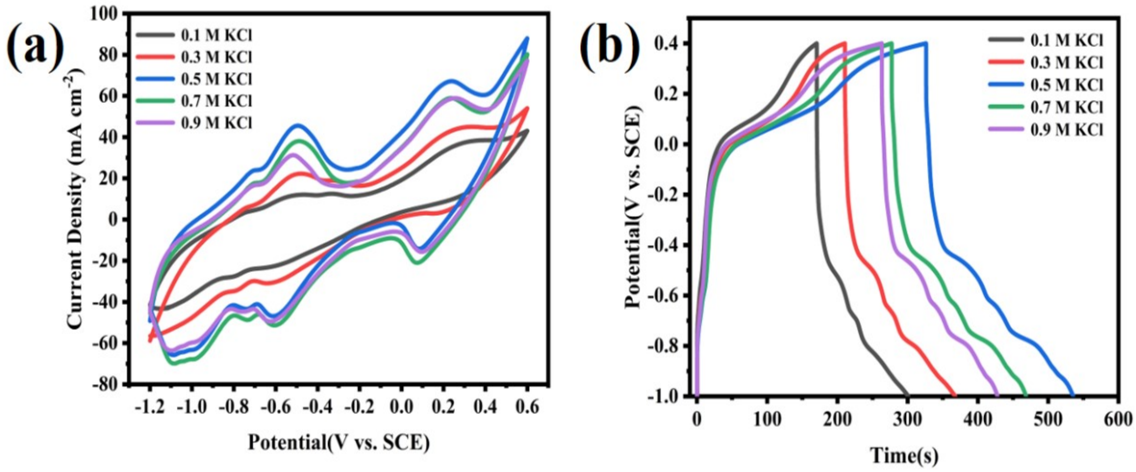

Fig.S6. Electrochemical properties of Cu@N-C-600 with different concentrations of KCl in the electrolyte. (a)CV curves at scan rate of 20 mV s^{-1} and (b)GCD curves at current density of 20 mA cm^{-2}.

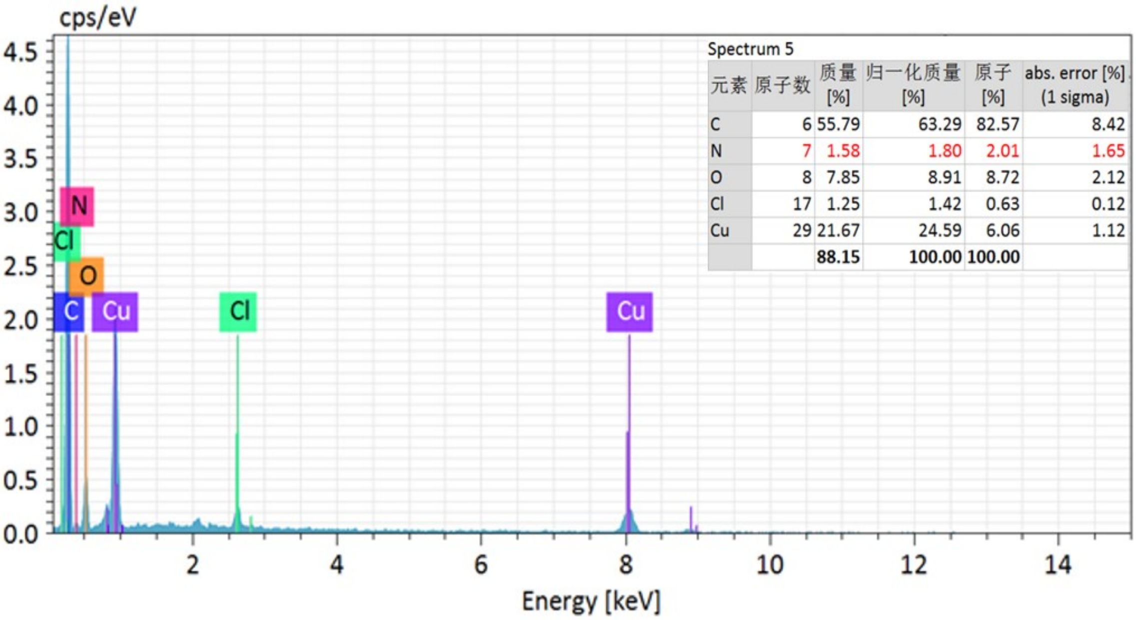

Fig.S7. EDS spectrum of Cu@N-C-600.

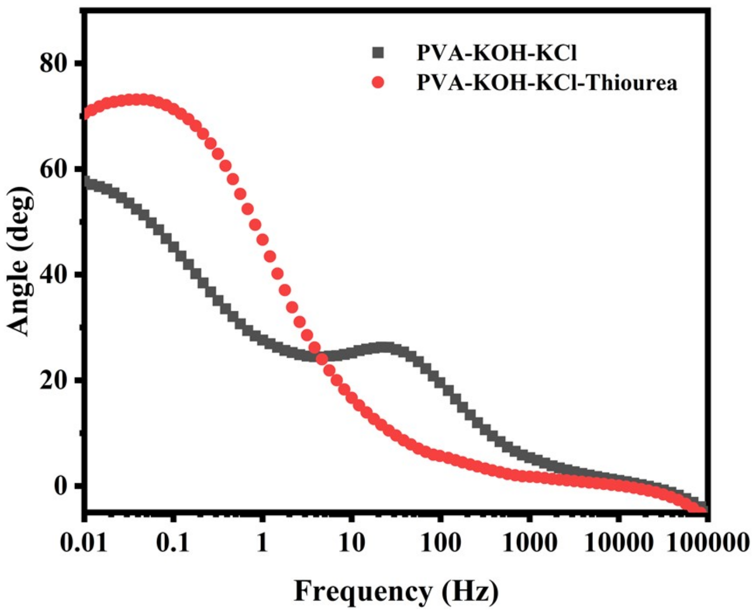

Fig.S8. The bode plot of Cu@N-C-600 // Cu@N-C-600 in different electrolyte.

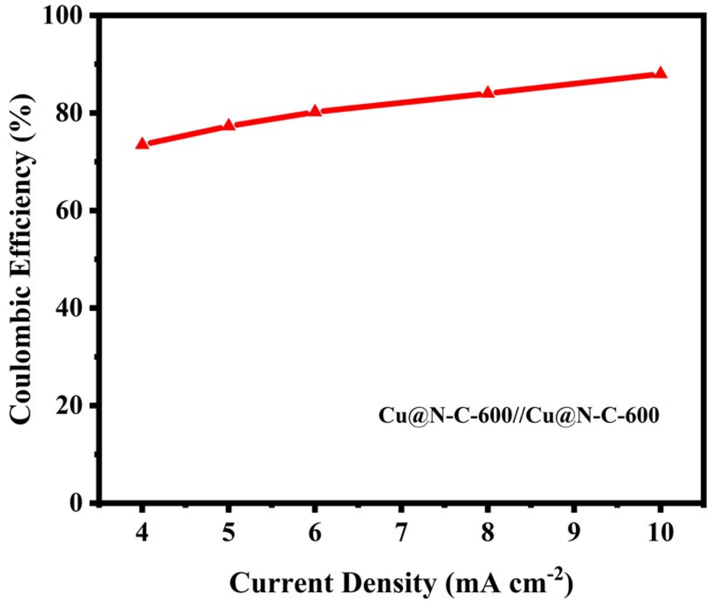

Fig.S9. Coulombic efficiency diagram for two-electrode system in different current density.

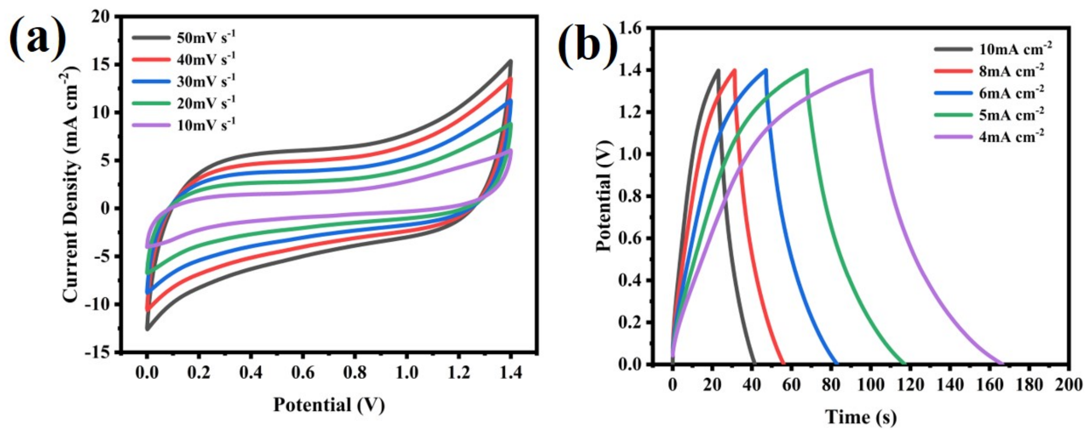

Fig.S10. Electrochemical test of Cu@N-C-600 // Cu@N-C-600 supercapacitor in PVA-KOH-KCl gel electrolyte (a)CV at different scan rate; (b)GCD curves at different current density.

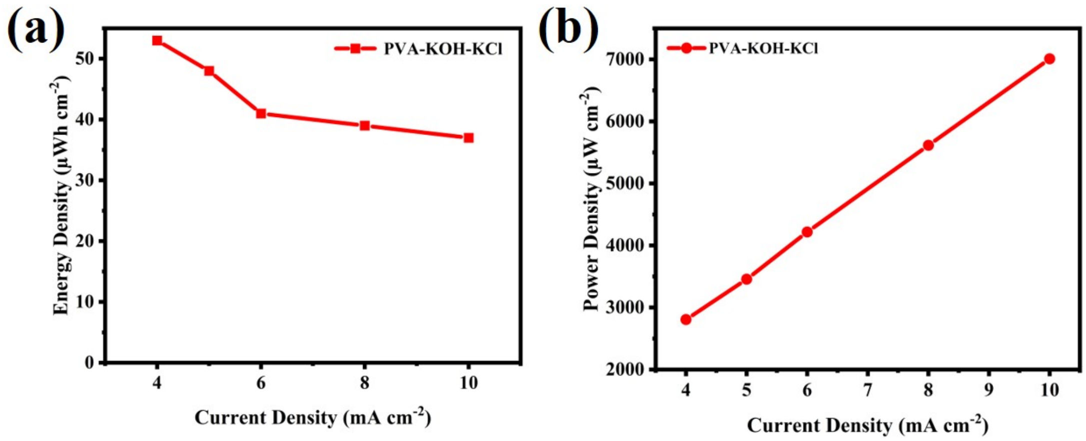

Fig.S11. Performance of Cu@N-C-600 // Cu@N-C-600 supercapacitor in PVA-KOH-KCl gel electrolyte. (a) energy density and (b)power density at different current densities.

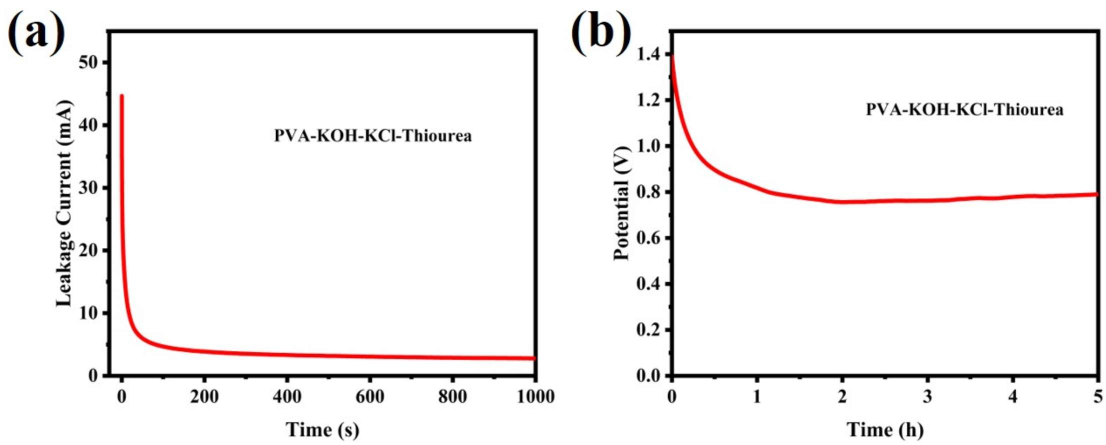

Fig. S12. Cu@N-C-600 SC in PVA-KOH-KCl-Thiourea gel electrolyte (a) leakage current and (b) self-discharge.

In order to further evaluate the stability of supercapacitors more accurately. The floating test was also applied to the supercapacitors. Simply put, the Cu@N-C-600 samples were performed between 0-1.4V utilizing a constant current density of 5 mA cm-2. Every 2h of adding, three GCD cycles were applied. Then, the specific capacitance was calculated from the first and third discharging time, respectively.

These sequences were repeated 20 times, a total floating time of 40h. And the results are shown below.

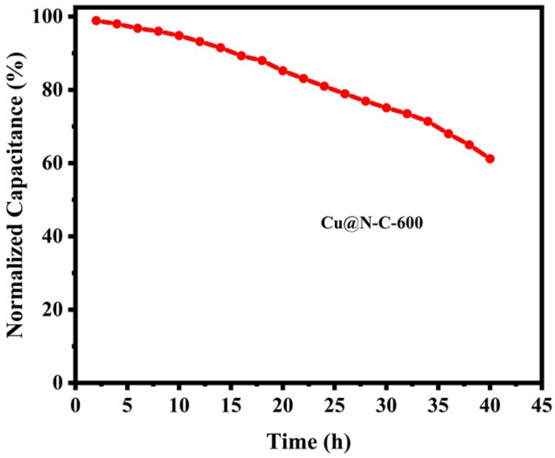

Fig. S13. The floating test of the Cu@N-C-600//Cu@N-C-600.

[1] W. Li, X. Wang, N. Zhang, M. Ma, Strong and Robust Polyaniline-Based Supramolecular Hydrogels for Flexible Supercapacitors, Angew. Che. Int. Ed. 55 (2016) 9196-9201.

[2] W. Li, H. Lu, N. Zhang, M. Ma, Enhancing the Properties of Conductive Polymer Hydrogels by Freeze–Thaw Cycles for High-Performance Flexible Supercapacitors, ACS Appl.Mater. Inter. 9 (2017) 20142-20149.