Electronic Supplementary Material (ESI) for RSC Advances.

Realizing high performance flexible supercapacitors by electrode modification

Tong Xia,[a] Depeng Zhao,[a] Qing Xia,[a] Ahmad Umar[c], Xiang Wu[a,b,*]

[a]School of Materials Science and Engineering, Shenyang University of Technology, Shenyang 110870, P. R. China

[b]Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, P. R. China

[c]Promising Centre for Sensors and Electronic Devices (PCSED), Department of Chemistry, College of Science and Arts, Najran University, Najran 11001, Saudi Arabia

[*]Correspondences should be addressed: wuxiang05@163.com;wuxiang05@sut.edu.cn

Experimental

In a typical experiment, 0.3 g $Ni(NO_3)_2 \cdot 6H_2O$, 0.8732 g $Co(NO_3)_2 \cdot 6H_2O$, 0.3 g NH_4F and 0.6 g urea were successively dissolved in 70 mL deionized water. After continuous stirring, a piece of pre-treated nickel foam and the above mixed solution was put into an autoclave and heated at 160 ^oC for 12 h. Then the obtained samples were taken out and washed with deionized water and alcohol, respectively. After that 0.4804 g $Na_2S \cdot 9H_2O$ was added into 60 mL deionized water and stirring for 10 min. Then the prepared Ni-Co precursor and the mentioned solution was poured into an autoclave and heat it at 140 ^oC for 6 h to obtain $NiCo_2S_4$ sample.

$NiCo_2S_4$@PPy composite material was also prepared by an electrodeposition process. In a three-electrode system, the prepared $NiCo_2S_4$ sample was used as working electrode, Pt sheet as counter electrode, and Ag/AgCl as reference one. In a typical procedure, 1.5 g of p-toluenesulfonic acid and 1 mL of pyrrole monomer were added to 100 mL of deionized water. Then a layer of PPy film was deposited on the surface of Ni-Co precursor at 0.8 V. The deposition time is 30 s, 50 s and 70 s. Finally, an asymmetric supercapacitor was assembled. The detailed preparing process is the similar to previous report.

The asymmetric supercapacitor consists of a positive electrode ($NiCo_2S_4$@PPy-50 material), a negative electrode (activated carbon), and a diaphragm (NKK paper). The negative electrode material was prepared from AC, carbon black and polyvinylidene fluoride in the mass ratio of 7:2:1.

When the temperature rises to 50 ^oC, 2 g of polyvinyl alcohol (PVA) powder was

added into 23 ml of deionized water in a small amount, and stirred at 95 ^{o}C for 1 h. Then adding 2 g of KOH into 7 ml of deionized water, and after stirring evenly, the KOH solution was put into the PVA solution drop by drop to obtain an electrolyte. After that, the prepared positive and negative materials were put into the electrolyte for 10 min. Finally, the diaphragm was placed between the two motor materials to make an asymmetric supercapacitor.[27]

The mass of the positive and negative active substances can be calculated according to the formula:

$$m_+ / m_- = C_-\Delta V_- / (C_+\Delta V_+) \quad (S1)$$

where m_+, m_- are the mass of positive and negative active substances, respectively, C_+, C_- are the mass capacitance, and ΔV_+, ΔV_- are the voltage window.

Scanning electron microscope (SEM; Gemini SEM 300-71-31) and transmission electron microscope (TEM, JEM-2100 PLUS) are used to observe the microscopic morphology of the synthesized samples. The composition and structure information of the sample was studied by X-ray diffractometer (XRD, 7000, Shimadzu, 40 kV, Cu Kα, λ = 0.1541 nm). The elemental composite and chemical valences of the synthesized products can be obtained by X-ray spectrometry (XPS, ESCALAB 250 Xi, Thermo Scientific) and Fourier Transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet iZ10)

Electrochemical performance testing of the samples was performed by a CHI660E electrochemical workstation. Cyclic voltammetry (CV) curves, constant current charging/discharging (GCD) and electrochemical impedance spectroscopy

(EIS) were conducted with the synthetic products as working electrodes, Hg/HgO as reference electrodes and Pt sheets as counter ones in 3 M KOH electrolyte. The mass capacitance (C), energy density (E) and power density (P) of the product can be obtained by the following equations:

$$C = I\Delta t/m \quad \text{(S2)}$$

$$E = 1/2CV^2 \quad \text{(S3)}$$

$$P = E/\Delta t \quad \text{(S4)}$$

where I represents discharge current, Δt is discharge time, m represents the mass loading of the sample, and V is the voltage window.

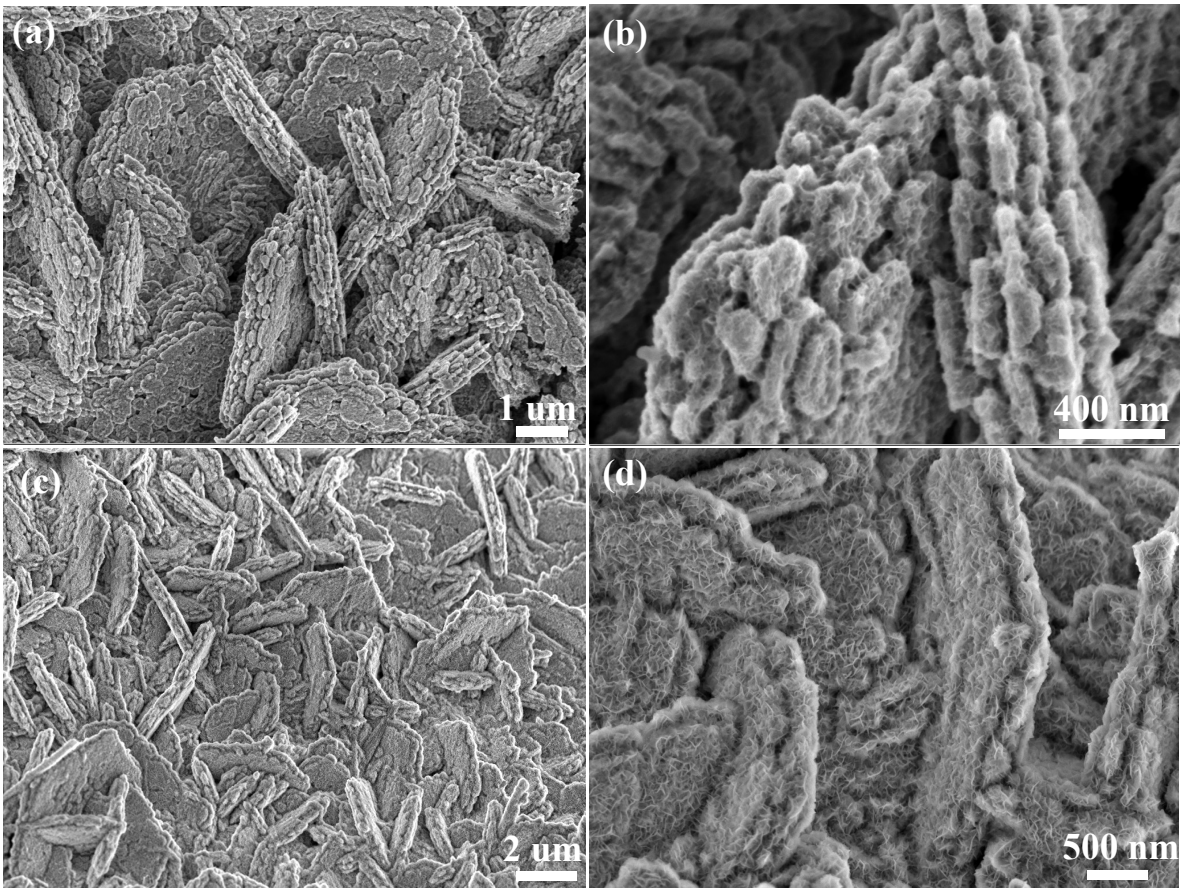

Fig. S1 SEM images of products (a-b) $NiCo_2S_4$@PPy-30 (c-d) $NiCo_2S_4$@PPy-70

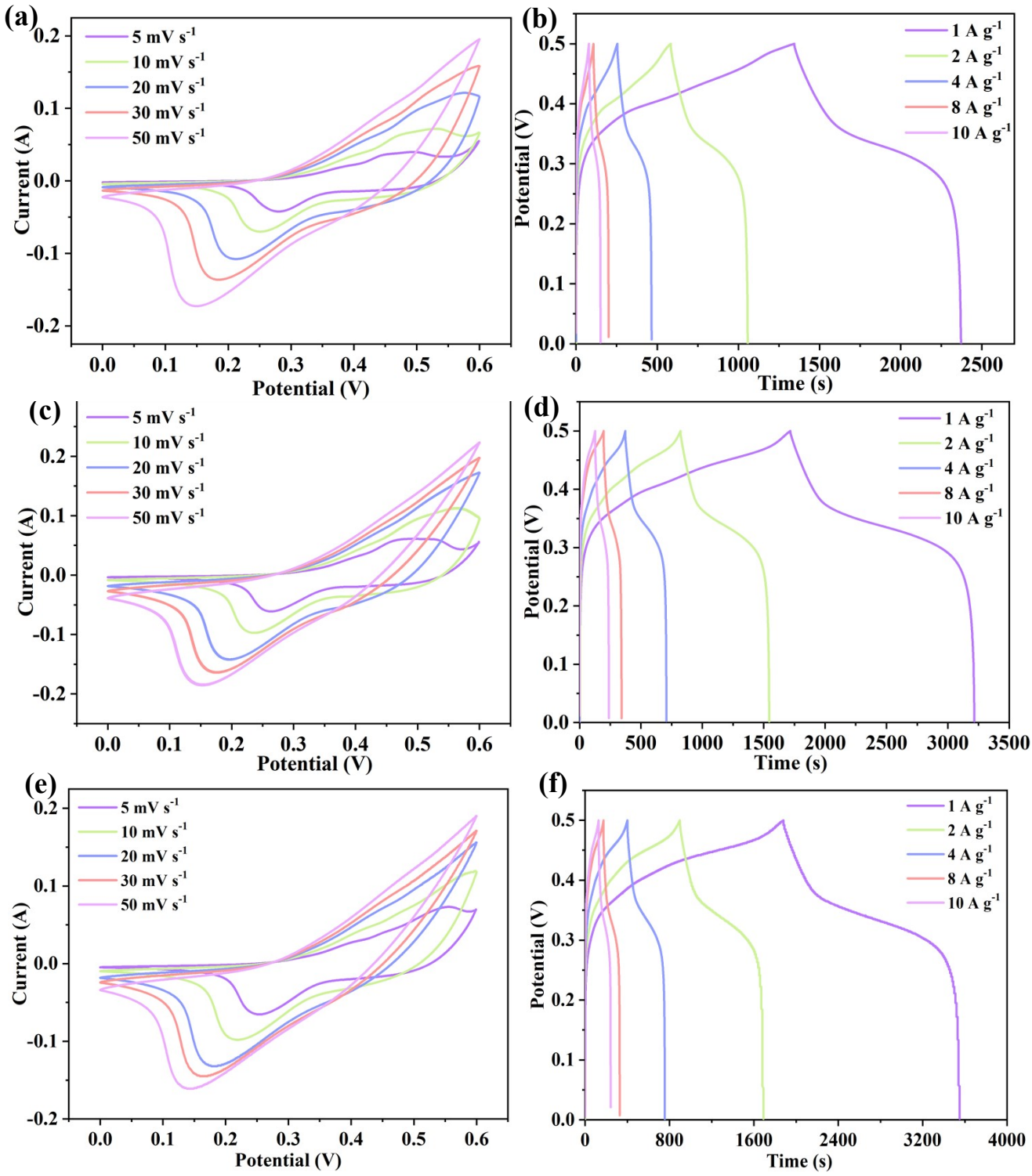

Fig. S2 Electrochemical performance (a, c, e) CV curves (b, d, f) GCD curves

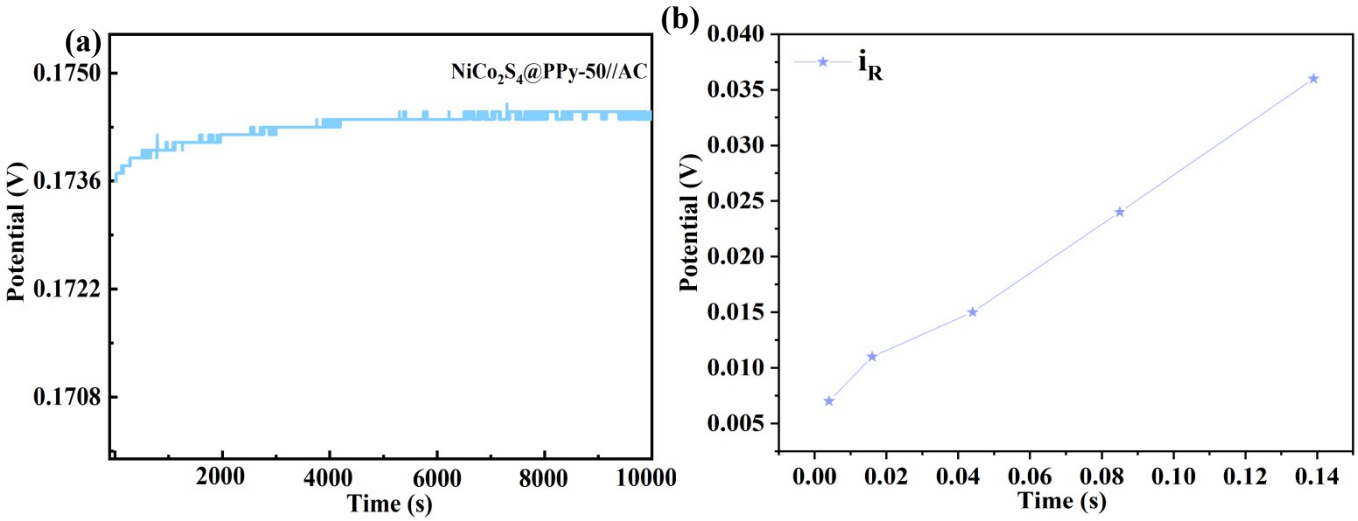

Fig. S3 (a) Cycling curve of $NiCo_2S_4$@PPy-50//AC (b) i_R diagram

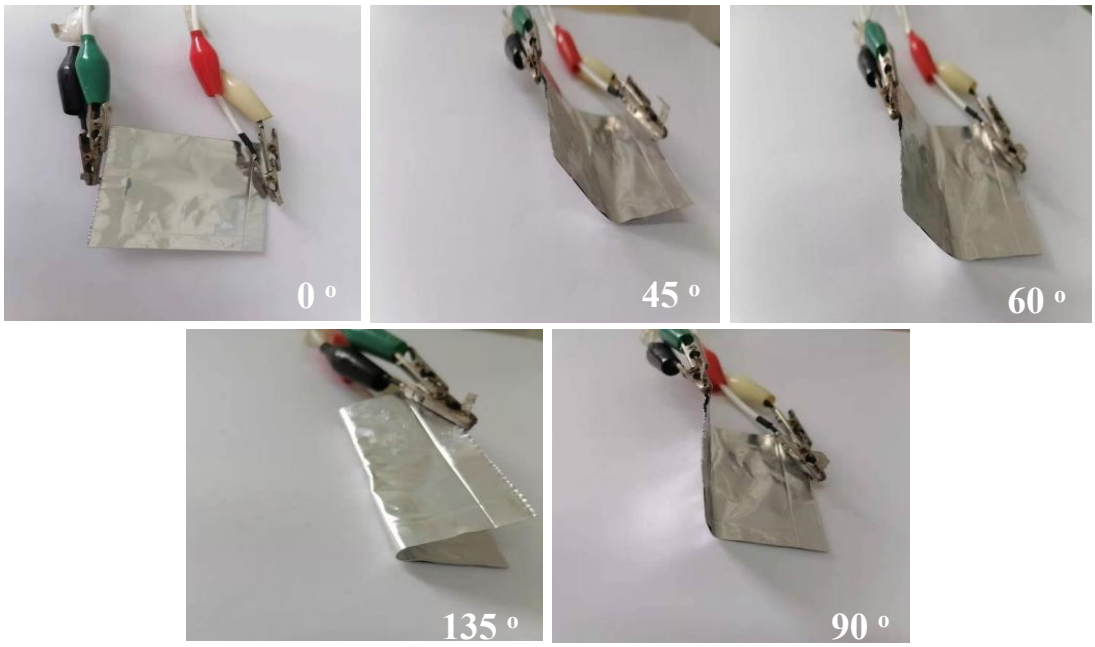

Fig. S4 Digital photos of the flexible device