In-situ Firmly Anchor Polypyrrole on NiV-LDHs for Efficient Aqueous-system Asymmetric Supercapacitors

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1. Experimental section

1.1. Preparation of NiV-LDHs, PPY and PPY@NiV-LDHs-X (X=1, 3, 6)

Chemical reagents were KOH, Acetylene black, $NiCl_2 \cdot 6H_2O$, VCl_3, Activated carbon (2000 m^2/g, 10 μm), Urea, C_4H_5N, Anhydrous Ethanol and $(NH_4)_2S_2O_8$. All the chemical reagents used above are purchased from Shanghai Aladdin Biochemical Technology Co., LTD. Deionized water is lab-made.

Preparation of NiV-LDHs: 0.40 g VCl_3, 0.94 g Urea and 1.78 g $NiCl_2 \cdot 6H_2O$ were evenly dispersed in a PTFE lining containing 80 mL ultra-pure water, then the PTFE lining was sealed in a high-pressure reactor and the reaction was carried out for 12 h at 120 °C. Whereafter, NiV-LDHs were obtained by centrifugal drying.

Preparation of PPY: The preparation of polypyrrole (PPY) at room temperature was investigated by referring to the reported literature [1]. For the preparation of **solution A**: Weigh 3.20 g ammonium persulfate $((NH_4)_2S_2O_8)$ and dissolve evenly in 20 mL deionized water. For the preparation of **solution B**: 1 mL of pyrrole (C_4H_5N) is uniformly dissolved in 50 mL of deionized water and 50 mL of anhydrous ethanol. The **solution A** is then added drop by drop to **solution B** and mixed evenly. The mixed solution is placed at room temperature and kept away from light for 24 h. After stirring, let it sit for 6 h, and finally centrifuge, dry, grind and collect polypyrrole (PPY).

Preparation of PPY@NiV-LDHs-X (X=1, 3, 6): For the preparation of **solution A**: Weigh 3.20 g ammonium persulfate $((NH_4)_2S_2O_8)$ and dissolve evenly in 20 mL deionized water. For the preparation of **solution C**: 1 mL of pyrrole (C_4H_5N) and 0.076 g NiV-LDHs are uniformly dissolved in 50 mL of deionized water and 50 mL of anhydrous ethanol. The **solution A** is then added drop by drop to **solution C** and mixed evenly. The mixed solution is placed at room temperature and kept away from light for 24 h. After stirring, let it sit for 6 h, and finally centrifuge, dry, grind and collect PPY@NiV-LDHs-1. According to the process of preparing PPY@NiV-LDHs-1, PPY@NiV-LDHs-3 material was finally obtained when the amount of NiV-LDHs used in the preparation of **solution C** was 0.228 g. According to the process of preparing PPY@NiV-LDHs-1, PPY@NiV-LDHs-6 material was finally obtained when the amount of NiV-LDHs used in the preparation of **solution C** was 0.456 g.

1.2. Characterizations

Using the full automatic fast surface and porosity analysis system (ASAP 2020 M, China), the nitrogen adsorption-desorption capacity, pore size distribution and specific surface area (S_{BET}) of the PPY@NiV-LDHs-3, PPY and NiV-LDHs were compared and analyzed by analyzing the Brunel-Emmett-Teller equations. The chemical compositions and valence of the elements in PPY@NiV-LDHs-3, PPY and NiV-LDHs materials were determined by XPS characterization on an X-ray photoelectron apparatus (ESCALAB 250Xi, USA) using monochromatic light (Al Kα) radiation source. At the scanning speed of $5°$ min^{-1}, the excitation current is 40 mA, the excitation voltage is 40 V, and the X-ray diffractometer (Rigaku, Smartlab SE, Japan) equipped with monochrome (Cu Kα) radiation point ($\lambda = 0.15418$ nm) is used, the crystal phase compositions of PPY@NiV-LDHs-X (X=1, 3, 6), PPY and NiV-LDHs were obtained. The Fourier transform infrared spectra of PPY@NiV-LDHs-X (X=1, 3, 6), PPY and NiV-LDHs were obtained on an infrared spectrometer (America, Thermo Electron, Nicolet Avatar 380), and make a comparative analysis. The zeta potential characterization of PPY@NiV-LDHs-3, PPY and NiV-LDHs materials were studied. The morphology and structure of the PPY@NiV-LDHs-3, PPY and NiV-LDHs materials were photographed using the Field Emission Scanning Electron Microscope (FESEM) and HRTEM (High Resolution Transmission Electron Microscope) instrument at 5 kV.

For the electrochemical performance test characterization of the three-electrode system and the two-electrode system, the detailed methods and corresponding calculation formula can be found in the previous work of our group [2]. Thereinto, the adhesive (PVDF (Polyvinylidene Fluoride) used in this study) was thoroughly mixed with NMP, acetylene black and electrode material in a ratio of 1:1:8, respectively. Evenly mixed and stirred for more than 12 h, and then coated on conductive carbon paper (JL-AQC-5C, 10*10*0.1 mm, Beijing Jinglongte Carbon Technology Co., LTD) and dried for more than 12 h to obtain the working electrode for testing.

2. Results and Discussion
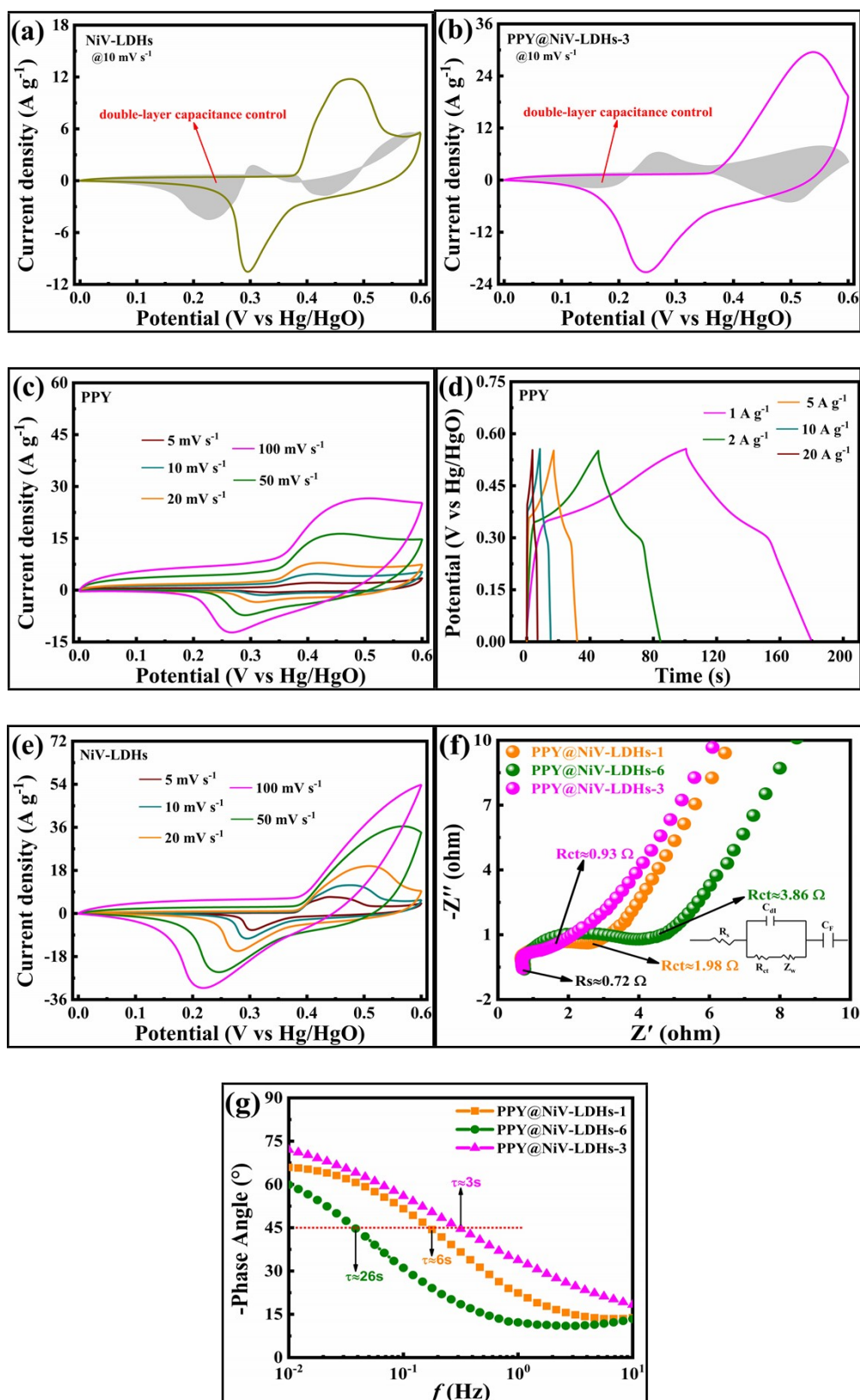
2.1. Three-Electrode System

Fig. S1. (a-b) By fitting the CV curves (10 mV s^{-1}) of the NiV-LDHs and PPY@NiV-LDHs-3, the contribution of the double-layer capacitance is obtained. **(c)** CV curves (5 to 100 mV s^{-1}) of the PPY. **(d)** GCD curves(1 to 20 A g^{-1}) of the PPY. **(e)** CV curves (5 to 100 mV s^{-1}) of the NiV-LDHs. **(f)** EIS curves of the PPY@NiV-LDHs-1,

PPY@NiV-LDHs-6 and PPY@NiV-LDHs-3. **(g)** Relationship between phase angle and frequency of PPY@NiV-LDHs-1, PPY@NiV-LDHs-6 and PPY@NiV-LDHs-3.

The actual mass of AC coated on the electrode sheet was 3.0 mg, and the cyclic volt-ampere characteristic curve of commercial activated carbon (AC) was tested and drawn. The scanning rate (5 mV s^{-1} to 100 mV s^{-1}) of the cyclic volt-ampere characteristic curve little by little enlarge, and the rectangle-like (one of the characteristics of double-layer capacitor materials) area enclosed by the cyclic volt-ampere characteristic curve also gradually increased, as shown in **Fig. S2a**. The GCD graphs of commercial activated carbon was tested and drawn (**Fig. S2b**). The current density (1 A g^{-1} to 20 A g^{-1}) of the GCD graphs little by little enlarge, while the area of the isosceles triangle enclosed (one of the characteristics of double-layer capacitor materials) by the GCD graphs gradually decreased. Based on the original data of the GCD graphs of commercial activated carbon obtained from the test, combined with the calculation formula of the mass specific capacity of the double electric layer capacitor material, the mass specific capacity bar chart of commercial activated carbon (AC) was calculated and drawn, as shown in **Fig. S2c**. The electrochemical impedance diagram of commercial activated carbon (AC) was tested and drawn, and the electrochemical impedance (Rct) of AC was ignored here (**Fig. S2d**).
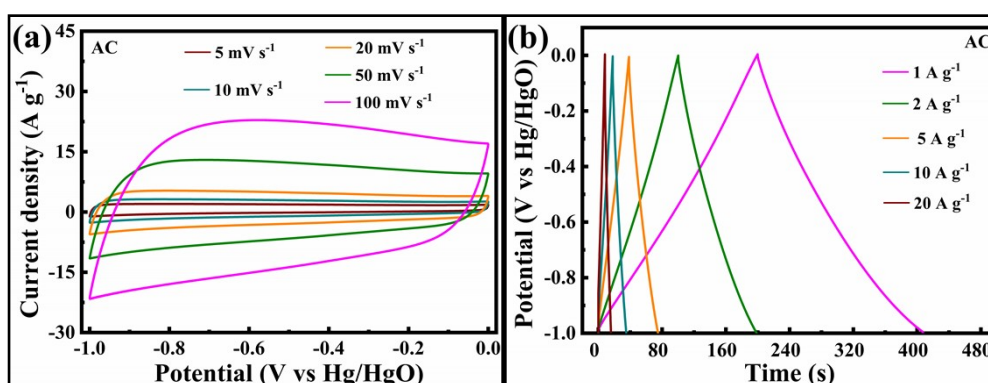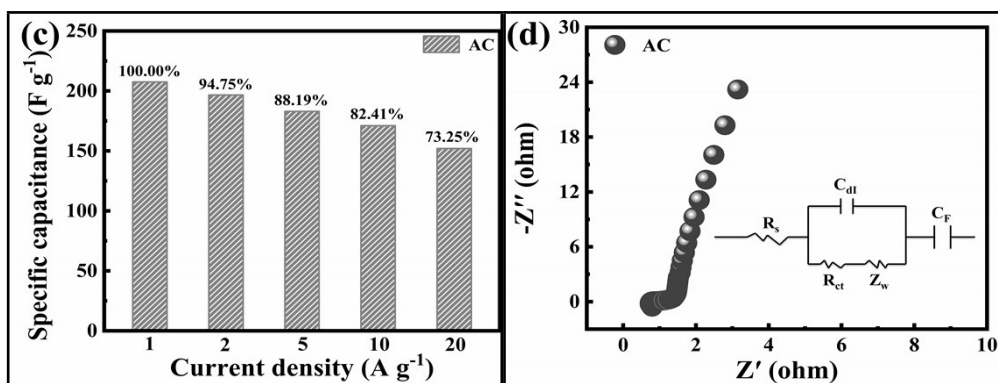
Fig. S2. (a) CV graphs of AC at 5 mV s^{-1} to 100 mV s^{-1}. **(b)** GCD graphs of AC (1 A g^{-1} to 20 A g^{-1}). **(c)** Mass-specific capacitance of AC. **(d)** EIS curves of AC.

References

[1] Y. Guo, S. Zhang, J. Wang, Z. Liu, Y. Liu, Facile preparation of high-performance cobalt–manganese layered double hydroxide/polypyrrole composite for battery-type asymmetric supercapacitors, J. Alloys Compd. 832 (2020) 154899.

[2] G. Liu, G. Wang, X. Guo, X. Hao, Z. Jin, Toilless sulfuration route to enhance the supercapacitor performance of nanoflower-like NiAl-layered double hydroxide, J. Electroanal. Chem. 916 (2022) 116368.