

Electronic Supplementary Information

Three-dimensional printing of black phosphorous/ polypyrrole electrode for energy storage using thermoreponsive ink

Ruizhe Xing,^{‡a} Yinqiang Xia,^{‡a} Renliang Huang,^{*b} Wei Qi,^{*ac}

Rongxin Su,^{ac} and Zhimin He^a

^a State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P.R. China

^b Tianjin Key Laboratory of Indoor Air Environmental Quality Control, School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, P.R. China

^c Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin University, Tianjin 300072, P.R. China

* Author to whom correspondence should be addressed:

tjuhrl@tju.edu.cn (R.H.), qiwei@tju.edu.cn (W.Q.)

‡ Ruizhe Xing and Yinqiang Xia contributed equally to this work.

1. Materials and Methods

1.1 Materials

Hexadecyltrimethylammonium bromide (CTAB, 99%), N-methyl-2-pyrrolidinone (NMP, 99.5%), Pyrrole (99%), Ammonium persulfate (APS, 99.99%), and 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI, 97%) were purchased from Aladdin Reagent Company (Shanghai, China). Bulk BP (99.998%) was purchased from Nanjing XFNANO Materials Tech Co., Ltd. (Nanjing, China). Absolute Ethanol, Hydrochloric acid were purchased from Real & Lead Chemical (Tianjin, China). Pluronic® F127 was purchased from Sigma-Aldrich (St. Louis, USA). Ultrapure deionized (DI) water was produced by a Milli-Q water purification system (Millipore Corporation, Billerica, MA, USA). All chemicals are used without further purification.

1.2 Preparation of Pluronic F127 Stock Solution

An overhead stirrer was used to prepare the Pluronic F127 stock solution (30 wt %). Pluronic F127/water mixture was first set still at 0 °C for 1 h to facilitate the mixing and then stirred under 150 rpm for 24 h until the stock solution became transparent. The stock solution was stored at 4°C fridge for as least 24 h before use.

1.3 Preparation of Black Phosphorous Nanosheets

The BPNSs were synthesized via a top-down route using a simple liquid exfoliation technology. In brief, 5 mg of bulk BP powder was dispersed in 10 mL of NMP in a glass bottle and mixed by sonication for 20 min. Then, the mixture was sonicated with a sonic tip at 1000 Hz and 30% power for 6 hours, during which the ultrasound probe was alternatively turned on for 2 s and off for 4 s. After exfoliation, the resultant dispersion was centrifuged for 20 min at 2000 rpm to remove non-exfoliated bulk BP. The supernatant containing BPNSs was pipetted off gently and centrifuged at 4000 rpm for another 20 min to collect precipitated BPNS. The precipitate was repeatedly rinsed with water and re-suspended in F127 stock solution at 0 °C with different concentration. The final concentration of BPNS-F127 solution was determined by ICP-OES.

1.4 Preparation of Polypyrrole Nanoparticles

Pyrrole monomers were added into 5 mM CTAB aqueous solution at 0 °C to give pyrrole monomer concentration of 40 mM. Then 1 eq of APS was added into the above mixture to initiate the polymerization. The polymerization went on at 0 °C for 24 h under vigorous stirring. After reaction, the precipitates were filtrated and washed with DI water and ethanol alternately to thoroughly remove the residue CTAB, then left to dry at 50 °C, resulting in a black powder. The polypyrrole powder was further grounded and sieved through 1000# mesh before use.

1.5 BPNS/PPy Ink Preparation

The BPNS/PPy ink was prepared by mixing PPy powder with the BPNS-F127 stock solution at 0 °C. Afterwards, the ink was set in a vacuum box for defoaming for 30 min. The final BPNS content of the prepared inks varied between 0.2 and 1 mg mL⁻¹.

1.6 Printing

The prepared BPNS/PPy ink was then loaded into a 5 mL syringe with circulated cooling jacket made of wrapped silicone tube (i.d. 0.5 mm) and extruded from a 0.3 mm diameter nozzle on a 1 mm nickel foam or an ITO glass slide by pressurizing (2 psig) air into the syringe.

1.7 Postprocessing

The printed sample was directly frozen with liquid nitrogen and lyophilized at -50°C for further characterization.

1.8 Ink Rheology

The viscoelastic properties (G' , G'') were examined with oscillation mode with fixed strain of 0.1% and frequency of 1.0 Hz. The effect of the temperature was monitored with a temperature ramp with ramping rate of 5 °C/min.

1.9 Structure and Morphology Characterization

The morphologies of the as-prepared BPNS/PPy electrodes were observed by scanning electron microscope (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, JEOL, JEM-2100F). Elemental analysis was conducted with an

energy dispersive X-ray spectrometer (EDS) equipped in the S-4800 SEM at an accelerating voltage of 10 kV. X-ray diffraction (XRD, Bruker, D8 advance) and Raman spectrum (Renishaw, inVia reflex) were used to examine the structure characterization of BPNS/PPy electrodes.

1.10 Electrochemical Characterization

Electrochemical measurements including cyclic voltammetry (CV) curves, galvanostatic charging/discharging (GCD) curves, and electrochemical impedance spectroscopy (EIS) (100 kHz-0.01 Hz) were conducted by an electrochemical workstation (CHI 660e) using a three-electrode system in EMI-TFSI electrolyte. Lyophilized BPNS/PPy (10mmx10mmx5mm) on nickel foam was used as working electrode, platinum wire as counter electrode, and Ag/AgCl (3M NaCl) as the reference electrode respectively.

The specific capacitance (C_s , F g⁻¹) from CV was calculated according to Eq. S1:

$$C_{s,CV} = \frac{\int I dV}{2\nu m \Delta V} \quad \text{Eq. S1}$$

where I (A) is the current, ν (V s⁻¹) is the scan rate, V (V) is the working potential and m (g) is the electrode mass.

The specific capacitance (C_s , F g⁻¹), specific energy (Wh kg⁻¹) and power density (W kg⁻¹) from GCD were calculated according to Eq. S2-Eq. S5:

$$C_{s,GCD} = \frac{2I\Delta t}{m\Delta V} \quad \text{Eq. S2}$$

$$\text{Energy density} = \frac{1}{8} C_s \Delta V^2 \quad \text{Eq. S3}$$

$$\Delta V = V_{max} - IR_{drop} - V_{min} \quad \text{Eq. S4}$$

$$\text{Power density} = \frac{\text{Energy density}}{t_d} \quad \text{Eq. S5}$$

where m (g) is the electrode mass and t_d (s) is the total discharge time of the SC.

The EIS was performed at open circuit voltage (i.e., 0 V) within the frequency range of 10 mHz to 100 kHz and a 5 mV AC amplitude. The specific capacitance (C_s , F g⁻¹) from EIS was calculated according to Eq. S6:

$$C_{s,EIS} = \frac{2|\text{Im}(Z)|}{2\pi m f [(\text{Im}(Z))^2 + (\text{Re}(Z))^2]} \quad \text{Eq. S6}$$

where f is the operating frequency (Hz), and $\text{Im}(Z)$ and $\text{Re}(Z)$ (Ohm) are the imaginary and real parts of the total resistance, m (g) is the electrode mass. The relaxation time constant (τ_0), which separates the capacitive behavior and resistive behavior of the supercapacitor, was deduced from the frequency f_0 as Eq. S7:

$$\tau_0 = \frac{1}{f_0} \quad \text{Eq. S7}$$

where f_0 is the frequency at which 50% of the capacitance can be accessed.

2. Supplementary Figures

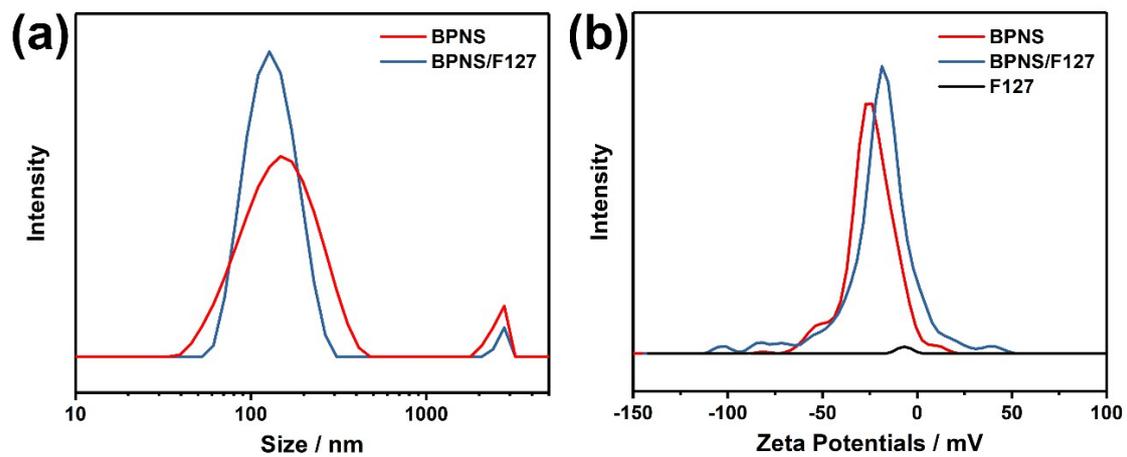


Fig. S1 (a) Dynamic Light Scattering (DLS) of BPNS solution and BPNS/F127 solution. (b) Zeta Potential test of the as-prepared inks with different composition.

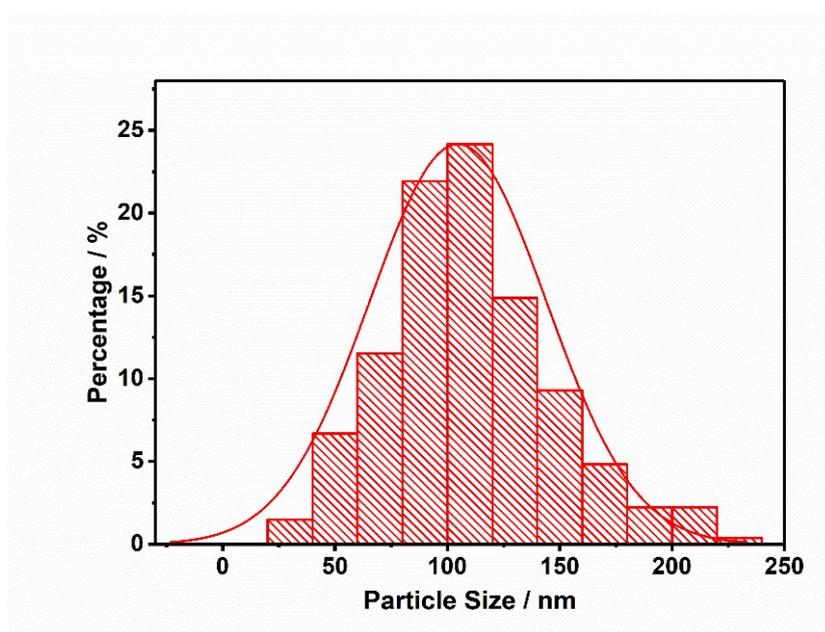


Fig. S2 Size distribution of the PPy nanoparticles.

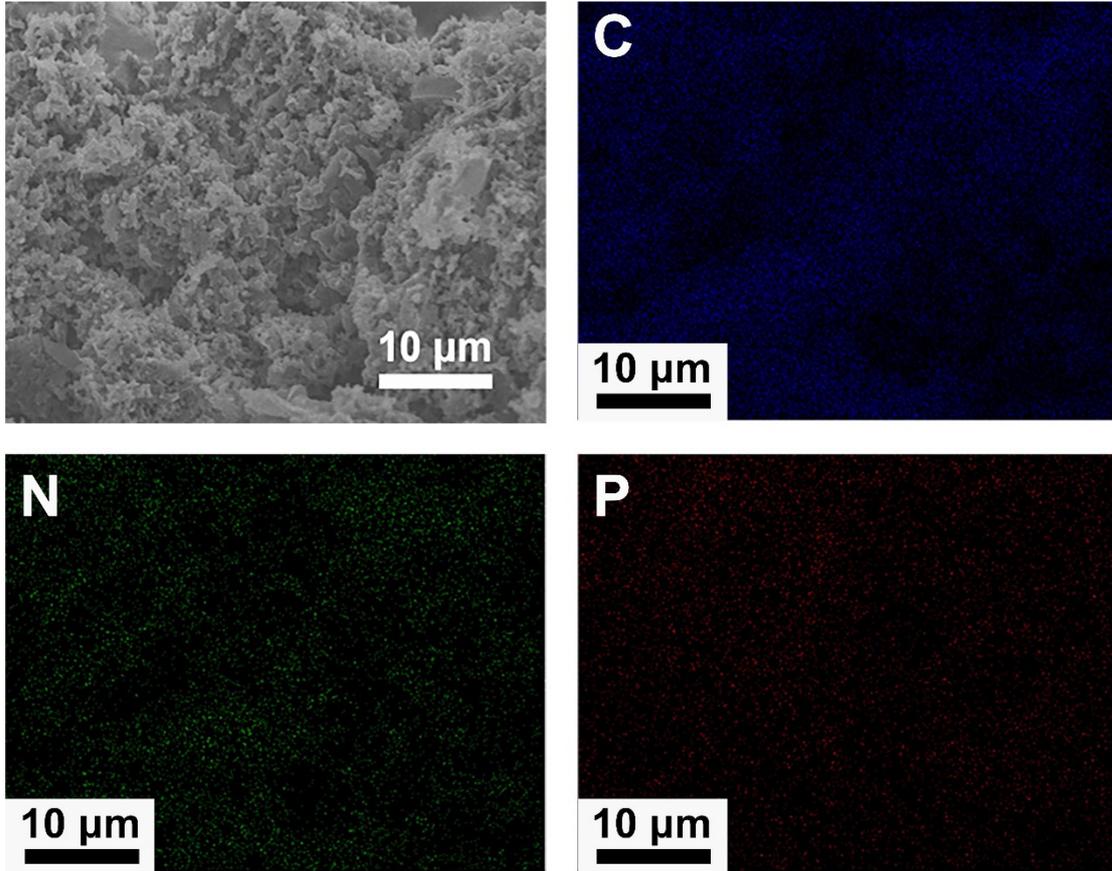


Fig. S3 The elemental distribution of the printed BPNS/PPy electrodes

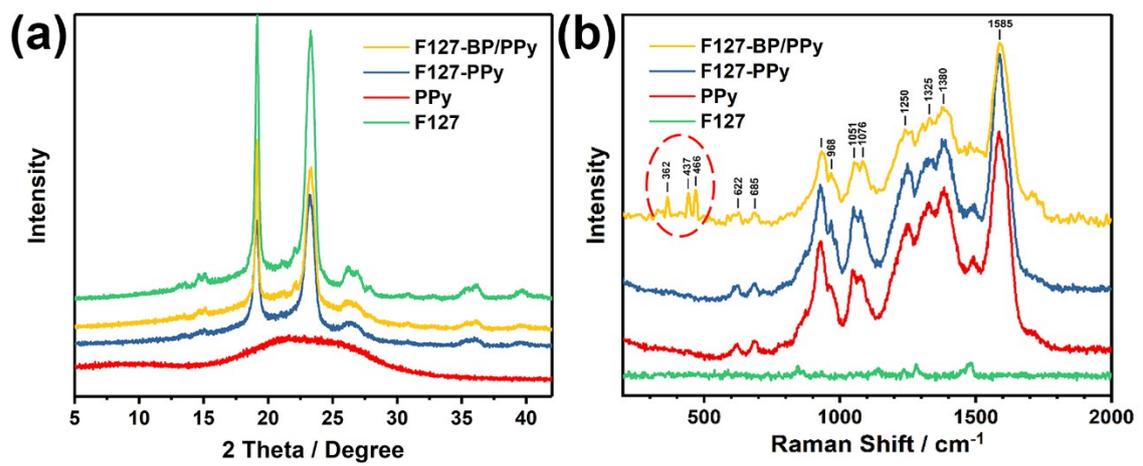


Fig. S4 The XRD patterns (a) and Raman spectra (b) of the as-prepared BPNS/PPy electrodes.

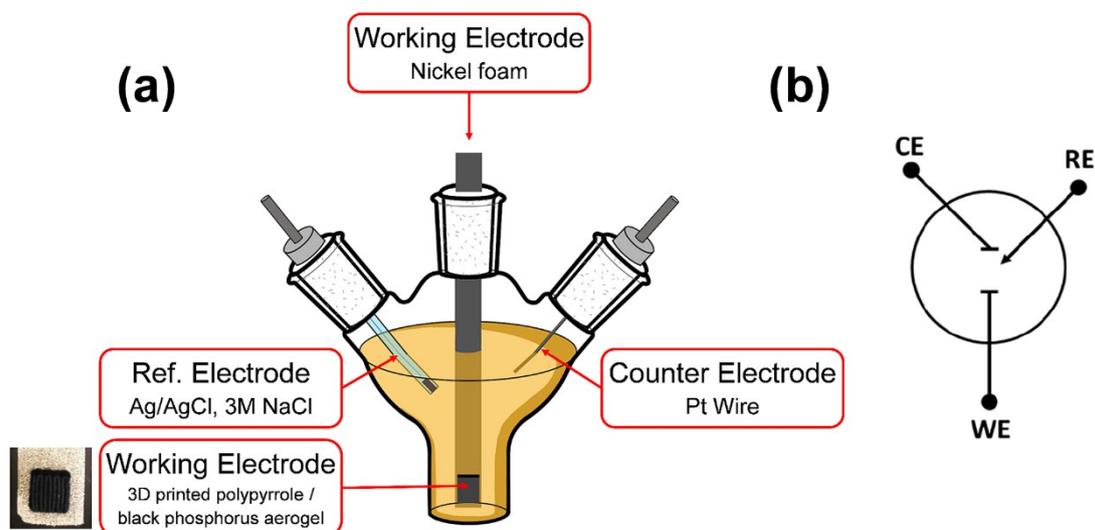


Fig. S5 Schematic illustration of the three-electrode system used for electrochemical characterization of the 3D printed BPNS/PPy micro-lattice grid electrode in EMI-TFSI electrolyte with: (a) detailed schematic diagram of the ψ -shaped glass/cuvette cell with inset depicting the employed 3D printed BP/PPy micro-lattice working electrode. (b) a simplified diagram of counter (CE), reference (RE) and working (WE) electrode setup.

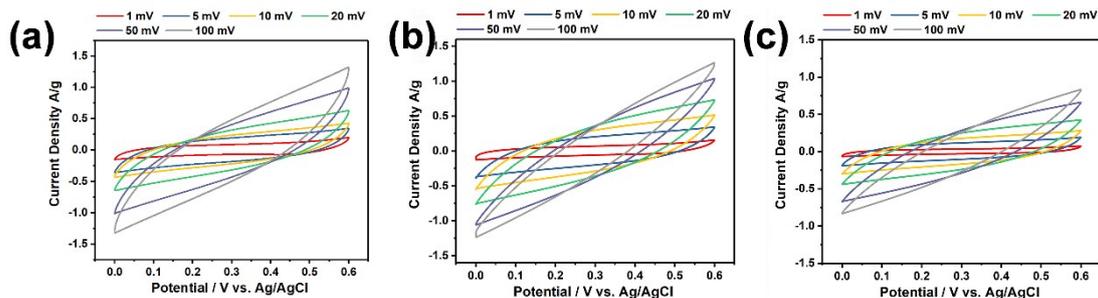


Fig. S6 CVs of the as-prepared BPNS/PPy electrodes with different BPNS concentration: (a) 0.972 mg mL⁻¹, (b) 0.673 mg mL⁻¹, (c) 0.326 mg mL⁻¹.

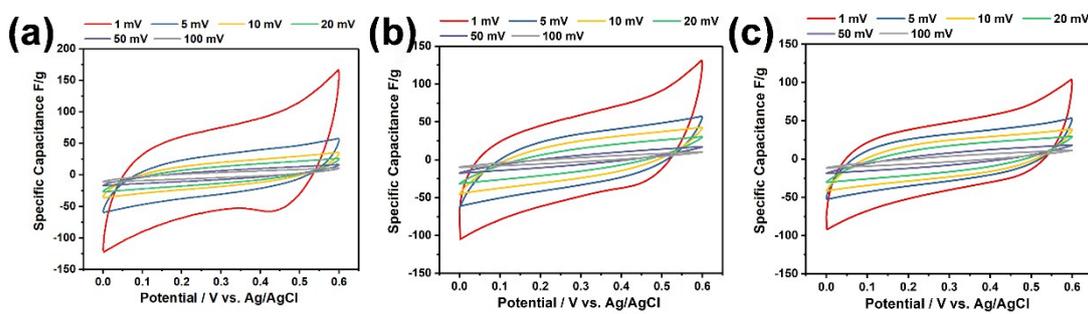


Fig. S7 Specific capacitance of the as-prepared BPNS/PPy electrodes obtained from CV scan with different BPNS concentration: (a) 0.972 mg mL⁻¹, (b) 0.673 mg mL⁻¹, (c) 0.326 mg mL⁻¹.

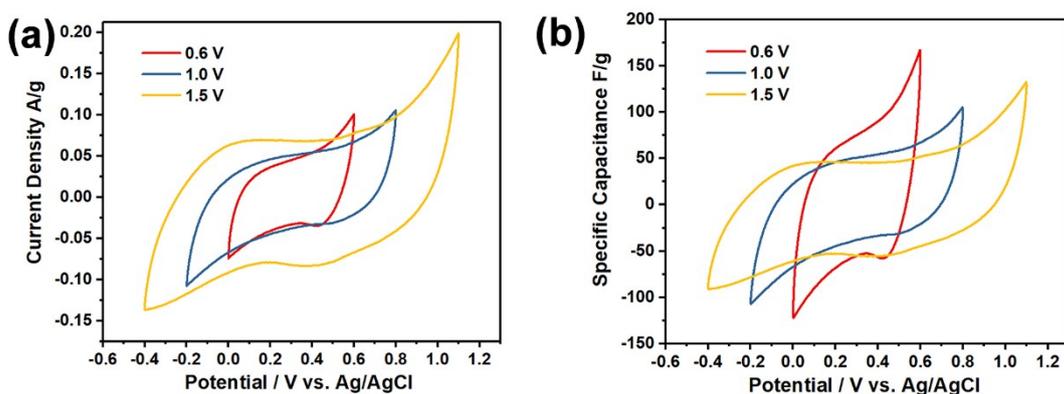


Fig. S8 (a) CV of BPNS/PPy electrodes recorded at a fixed scan rate of 1 mV s⁻¹ and with increasing operating potentials of 0.6, 1.0 and 1.5 V. (b) Specific capacitance derived from (a).

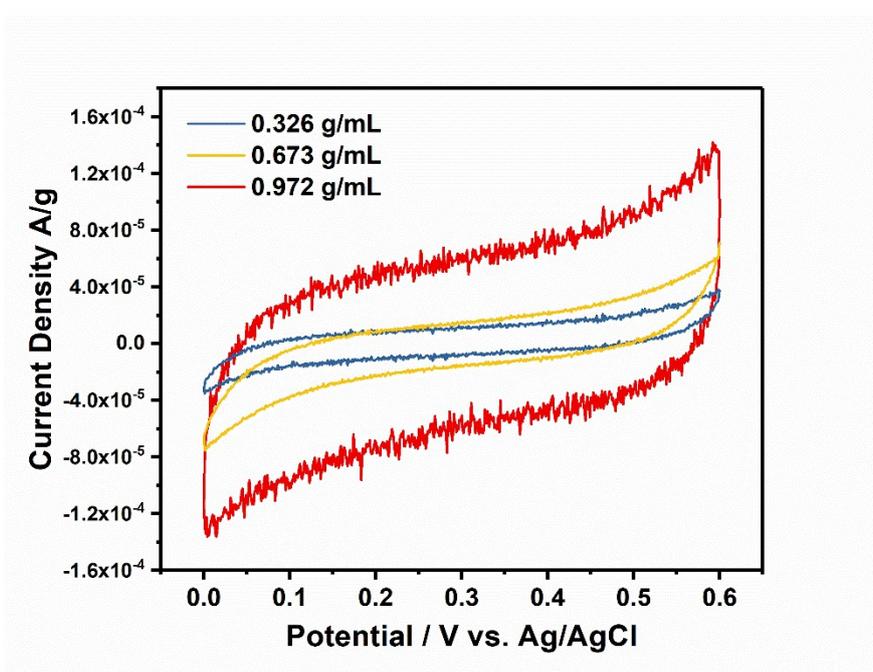


Fig. S9 CVs of the printed pure BPNS electrodes with different BPNS concentration of 0.972 mg mL⁻¹, 0.673 mg mL⁻¹ or 0.326 mg mL⁻¹

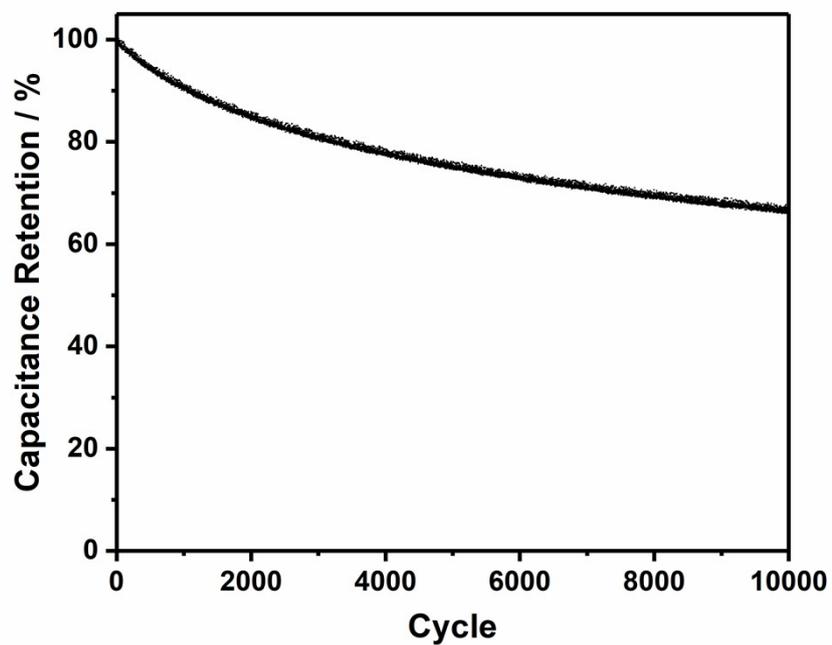


Fig. S10 Cycling stability of 10000 charging/discharging cycles at 0.1 A/g for printed pure PPy electrode.

3. Supplementary Tables

Table S1 Comparison of capacitance on recently reported polypyrrole composite materials

Materials	Specific Capacitance (F/g)	Loading Materials	No. of Cycles	Capacitance Retention %	Ref.
Polypyrrole and black phosphorous nanosheet	417	BPNS	10000	87	This work
Polypyrrole and graphene nanofiber	161	Graphene	5000	80	1
Polypyrrole and multilayered graphene nanosheet	165	Graphene	1000	92	2
CuS@polypyrrole nanoparticle	427	CuS NP	1000	88	3
Polypyrrole and carbon nanotube	221	CNT	5000	95	4
Polypyrrole and MoO ₃	125	MoO ₃ NP	600	83	5
Polypyrrole and graphene nanosheet	395	Graphene	5000	90	6
Graphene silver nanoparticles and polypyrrole	450	Ag NP	1000	92	7
Cu-TCPP MOFs and Polypyrrole	500	Cu-TCPP	3000	70	8
ZIF67 and Polypyrrole	284	ZIF-67	40000	100.7	9

References

1. K. Shu, Y. Chao, S. Chou, C. Wang, T. Zheng, S. Gambhir and G. G. Wallace, *ACS Appl. Mater. Interfaces*, 2018, **10**, 22031-22041.
2. S. Biswas and L. T. Drzal, *Chem. Mater.*, 2010, **22**, 5667-5671.
3. H. Peng, G. Ma, K. Sun, J. Mu, H. Wang and Z. Lei, *J. Mater. Chem. A*, 2014, **2**, 3303-3307.
4. X. Lu, H. Dou, C. Yuan, S. Yang, L. Hao, F. Zhang, L. Shen, L. Zhang and X. Zhang, *J. Power Sources*, 2012, **197**, 319-324.
5. Y. Liu, B. Zhang, Y. Yang, Z. Chang, Z. Wen and Y. Wu, *J. Mater. Chem. A*, 2013, **1**, 13582-13587.
6. Z. Qi, J. Ye, W. Chen, J. Biener, E. B. Duoss, C. M. Spadaccini, M. A. Worsley and C. Zhu, *Adv. Mater. Technol.*, 2018, **3**, 1800053.
7. P. K. Kalambate, R. A. Dar, S. P. Karna and A. K. Srivastava, *J. Power Sources*, 2015, **276**, 262-270.
8. H. Yao, F. Zhang, G. Zhang, H. Luo, L. Liu, M. Shen and Y. Yang, *Chem. Eng. J.*, 2018, **334**, 2547-2557.
9. Y. Liu, N. Xu, W. Chen, X. Wang, C. Sun and Z. Su, *Dalton T.*, 2018, **47**, 13472-13478.