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Electronic Supplementary Information for

Controlled Synergistic Strategy to Fabricate 3D-skeletal Hetero-nanosponges with High Performance for Flexible Energy Storage Applications

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Materials

Indole monomer (99% purity), ammonium persulphate (APS), and p-toluenesulfonic acid (p-TSA) were purchased from Sinopharm Chemical Reagent Co. Ltd, Shanghai, China. Chloroform (>99.5%) was acquired from Shanghai Lingfeng Chemical Reagent Co. Ltd. Polyethylene Oxide (PEO) (Mw = 400,000 g/mol) and Multi-walled CNTs were purchased from Sigma-Aldrich

Experimental

Pind was polymerized as described elsewhere.[1] Briefly, indole (0.1M) was added to in 50 ml of ethanol to make the monomer solution, which then was introduced into a nitrogen degassed reaction flask kept at 0 °C with a stirrer. 2.282 g (0.2 M) ammonium persulphate in distilled water was then dropwise added to the monomer solution. The reaction vessel was continued under stirring for 6 hrs at RT for complete polymerization. Finally, the polymer was washed for several times with ethanol and double distilled water before vacuum-drying at 60 °C for 24 hrs

The electrospinning solution was prepared with 1.85 wt/v% of Pind and P-TSA in 15 ml of chloroform stirred for 3 hrs. Finally, PEO (PEO:Pind=20:80) was added to the Pind solution and left stirring for 12 hrs. For the electrospraying solution, similar procedure above was followed except before addition of PEO, CNTs were first added in a 80:15:5 (Pind: CNT: PEO) ratio

Characterization

Nicolet™ 6700 spectrometer was used to obtain the Fourier transform infrared (FTIR) spectra of Pind powder and the nanosponges with samples in potassium bromide(KBr) pellets in the spectral range of 4000–500 cm^{-1}. X-ray diffraction (XRD) of Pind Powder and the nanosponges, CNTs, and PEO was probed using D/MAX 2550VB/PC diffractometer, Rigaku Tokyo, Japan.

Cyclic Voltammetry (CV) and Galvanostatic charge-discharge (GCD) tests were characterized with the help of an electrochemical workstation (CHI 660E) in three electrode setup in 1 M H_2SO_4. EIS test was employed with 5 mV AC amplitude and frequency range of 1 MHz–100 mHz. The specific capacitance values (C_s) in F g^{-1} from CV and GCD were calculated according to the equation (1) and (2) below:

$$C_s = {}^{1}\!/_{2}\frac{\int I(V)dV}{mv\Delta V} \qquad (1)$$

$$C_s = \frac{I\Delta t}{m\Delta V} \qquad (2)$$

where m (g) is the mass of the electrode active material, ΔV (V) is the is the potential window, v (V s^{-1}) is potential scan rate, discharging time Δt (s), and I(A) is the constant discharging current.

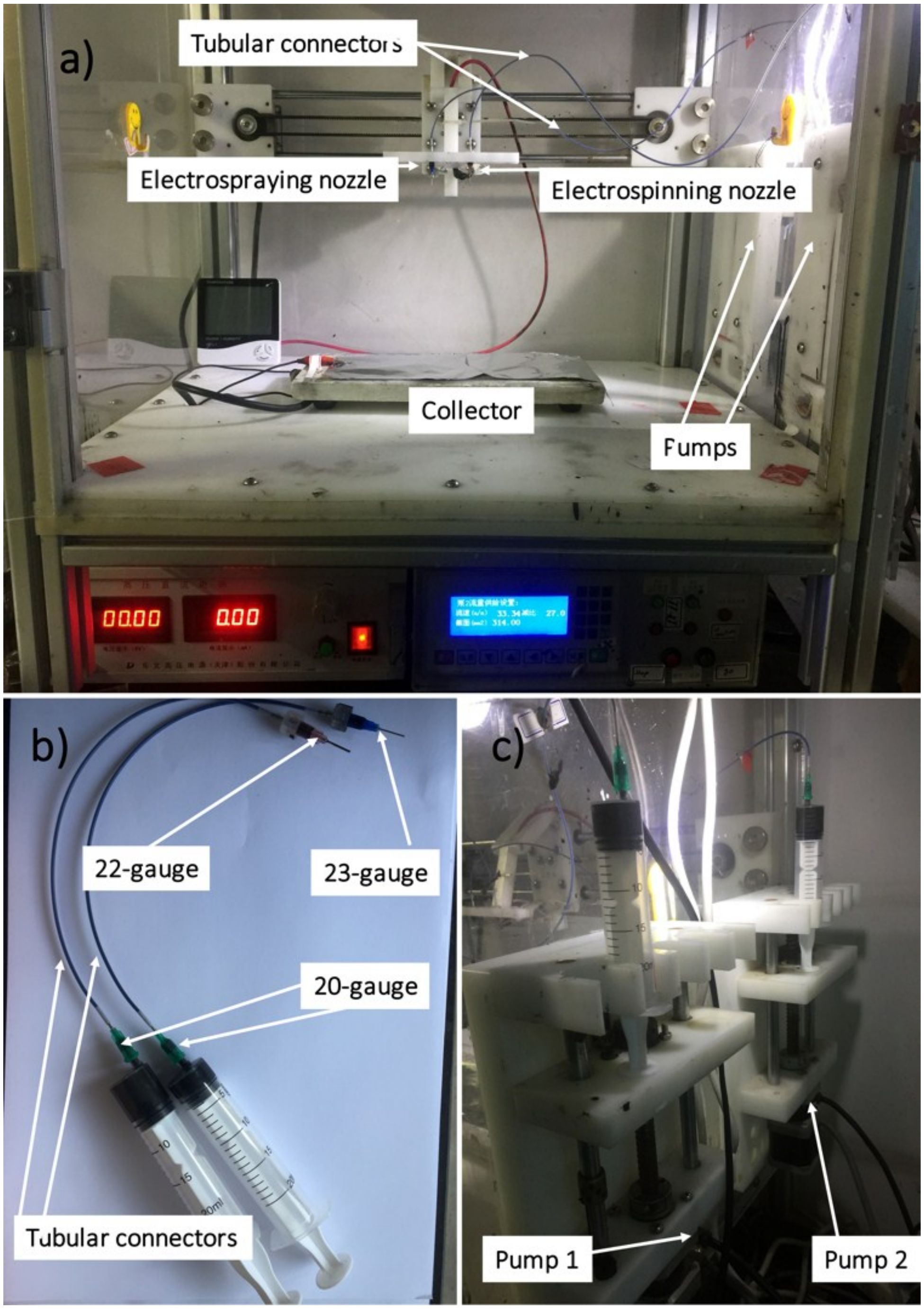

Fig. S1. Customized electrospinning/electrospraying machine. (a) Arrangement of the nozzles, pumps and collector. (b) Spinning solutions held in syringes with tubular connections of the electrospraying and electrospinning nozzles to the 20-gauge nozzles. C) Arrangement of pumps onto the machine.

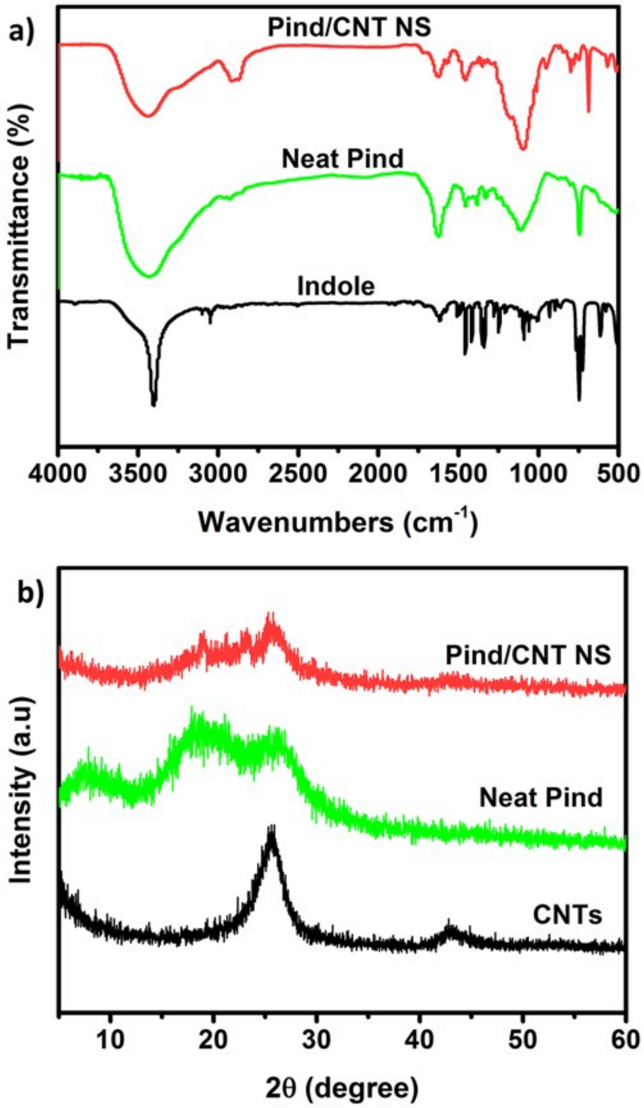

Fig. S2. a) FTIR spectra of CNTs, neat Pind and Pind/CNT NS and b) XRD curves of indole Pind, Pind/CNT NS.

The FTIR (**Fig. S2a**) confirmed the successful chemical polymerization of Pind with typical peaks at 3431 cm^{-1}, 1618 cm^{-1}, 1456 cm^{-1},1111 cm^{-1}, and 747 cm^{-1} which are ascribed to the existence of N-H, C=C, C-H, C-N and the benzene ring, respectively.[2-4] In the Pind/CNT NS FTIR spectra, the positions of polymer peaks were not too much altered, indicating a poor chemical interaction of active materials with PEO. Peaks at 747 cm^{-1} and 1456 cm^{-1} in the

Pind/CNT NS are observed to have diminished, which is due to the presence of PEO and introduction of CNTs in the Pind matrix. **Fig. S2b**, is the XRD curves of neat Pind, Pind/CNT NS, CNTs, and PEO. Typical peaks of Pind were observed at 2θ =18.75º and 26.16º, together with peak at 2θ =8.16º ascribed to periodic spacing between the dopant and the nitrogen atom of the neighboring Pind pyrrole ring.[4, 5] The Pind/CNT NS followed similar pattern like neat Pind, except its pattern was flatter with peaks 2θ =18.7º and 23.3º. Other peaks at 2θ =25.6º and faint peak at 2θ =42.8º also appeared in Pind/CNT NS. Peaks 2θ =18.7º and 23.3º are ascribed to the presence of PEO in the nanofiber as depicted by PEO XRD pattern with two sharp peaks at 18.8º and 23.2º. Moreover, peaks 2θ =25.6º and 42.8º are ascribed to pronounced graphite structure resulting from the interlayer spacing of the nanotubes and carbon atoms reflection of CNTs within nanosponges as depicted by CNTs XRD pattern too.[6]

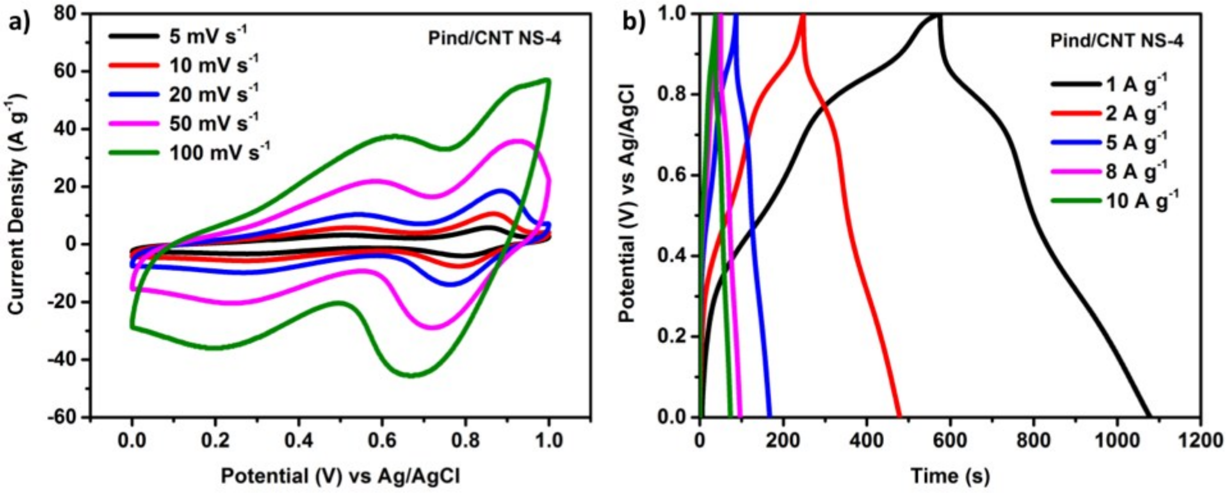

Fig. S3 a) CV and b) GCD curves of Pind/CNT NS-4

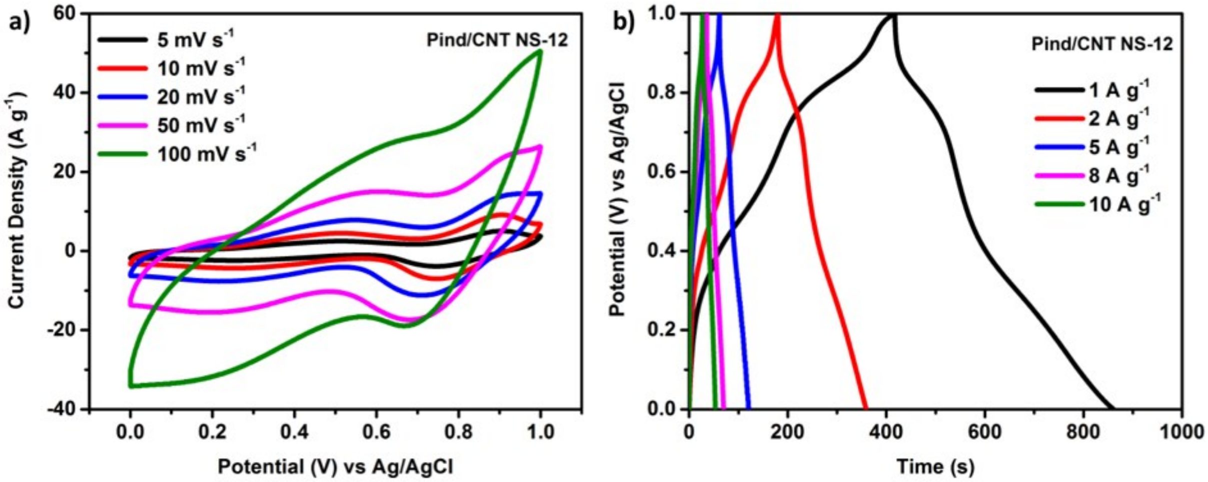

Fig. S4 a) CV and b) GCD curves of Pind/CNT NS-12

Supporting Information References

1. Q. Zhou, D. Zhu, X. Ma, D. Mo, F. Jiang, J. Xu and W. Zhou, *Electrochim. Acta*, 2016, **212**, 662-670.
2. H. Talbi, J. Ghanbaja, D. Billaud and B. Humbert, *Polymer*, 1997, **38**, 2099-2106.
3. R.-X. Wang, Y.-J. Fan, L. Wang, L.-N. Wu, S.-N. Sun and S.-G. Sun, *J. Power Sources*, 2015, **287**, 341-348.
4. M. Saleh, J. N. Tiwari, K. C. Kemp, M. Yousuf and K. S. Kim, *Environ. Sci. Technol.*, 2013, **47**, 5467-5473.
5. Q. Zhou, D. Zhu, X. Ma, J. Xu, W. Zhou and F. Zhao, *RSC Adv.*, 2016, **6**, 29840-29847.
6. D. B. Shinde, J. Debgupta, A. Kushwaha, M. Aslam and V. K. Pillai, *JACS*, 2011, **133**, 4168-4171.