Supporting Information

Controllable Design of Polypyrrole-Iron Oxide Nanocoral Architectures for Supercapacitors with Ultrahigh Cycling Stability

Chunping Xu,[+a] *Alain R. Puente-Santiago,*[+b] *Daily Rodríguez-Padrón,*[*b] *Alvaro Caballero,*[c] *Alina M. Balu,*[b] *Antonio A. Romero,*[b] *Mario J. Muñoz-Batista,*[b] *Rafael Luque*[*b,d]

[a] School of Food and Biological Engineering, Zhengzhou University of Light Industry Zhengzhou, Henan, 450002, PR China

[b] Departamento de Química Orgánica,Instituto de Química Fina y Nanoquímica, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal IV-A, Km 396, E14014, Cordoba, España. *D.R.P.: dailydggs@gmail.com, *R.L.: q62alsor@uco.es

[c] Departamento de Química Inorgánica e Ingeniería Química, Instituto de Química Fina y Nanoquímica, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal IV-A, Km 396, E14014, Cordoba, España.

[d]Peoples Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya str., 117198, Moscow, Russia.

‡These authors contributed equally to the work.

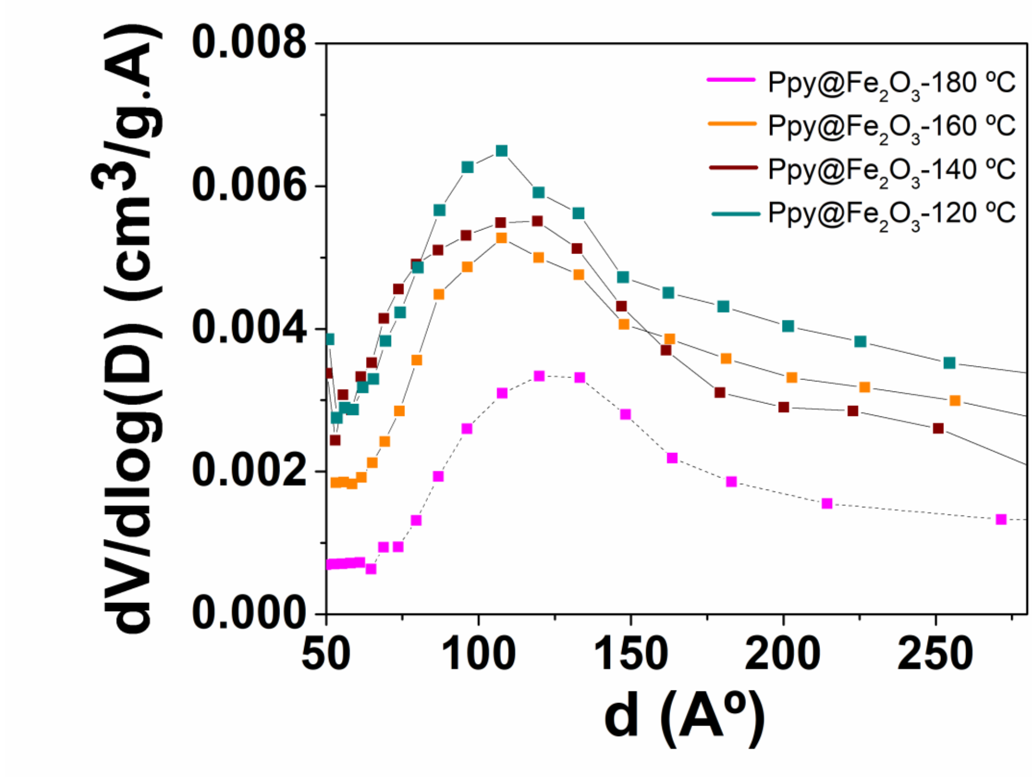

Figure S1. Pore diameter distribution of the polypyrrole-modified iron oxide nanomaterials.

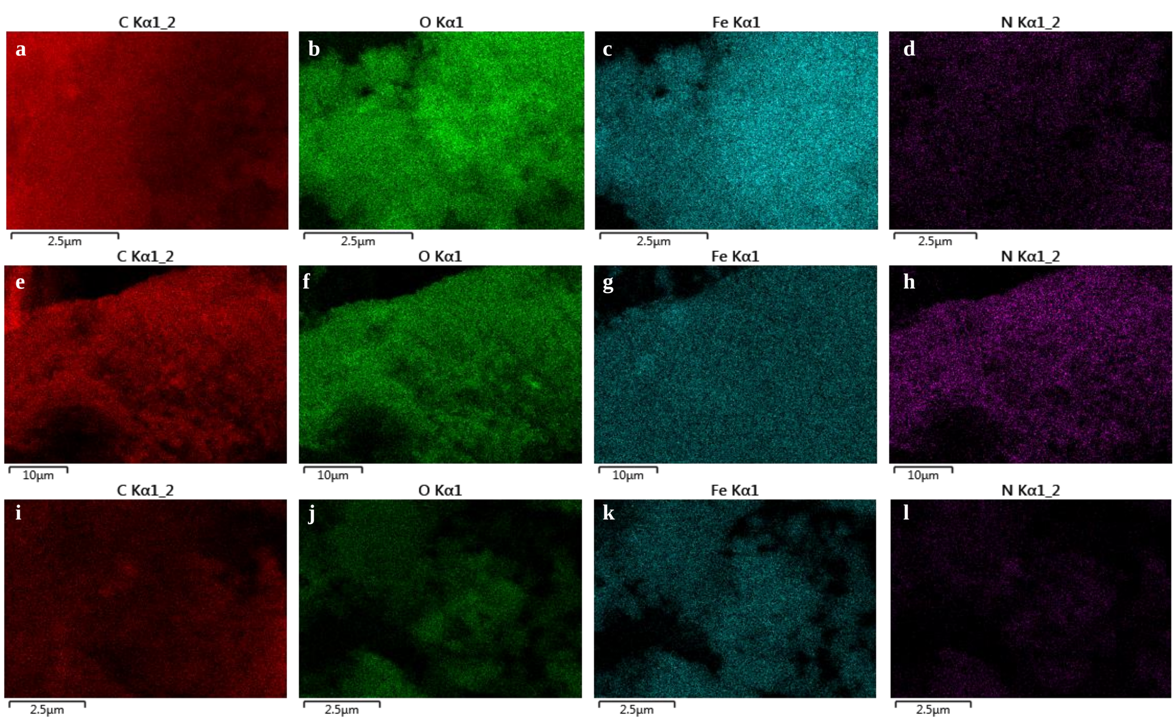

Figure S2. SEM-mapping images of (a-d) Ppy@Fe2O3-160 °C for C, O, Fe and N, (e-h) Ppy@Fe2O3-140 °C for C, O, Fe and N, (i-j) Ppy@Fe2O3-120 °C for C, O, Fe and N.

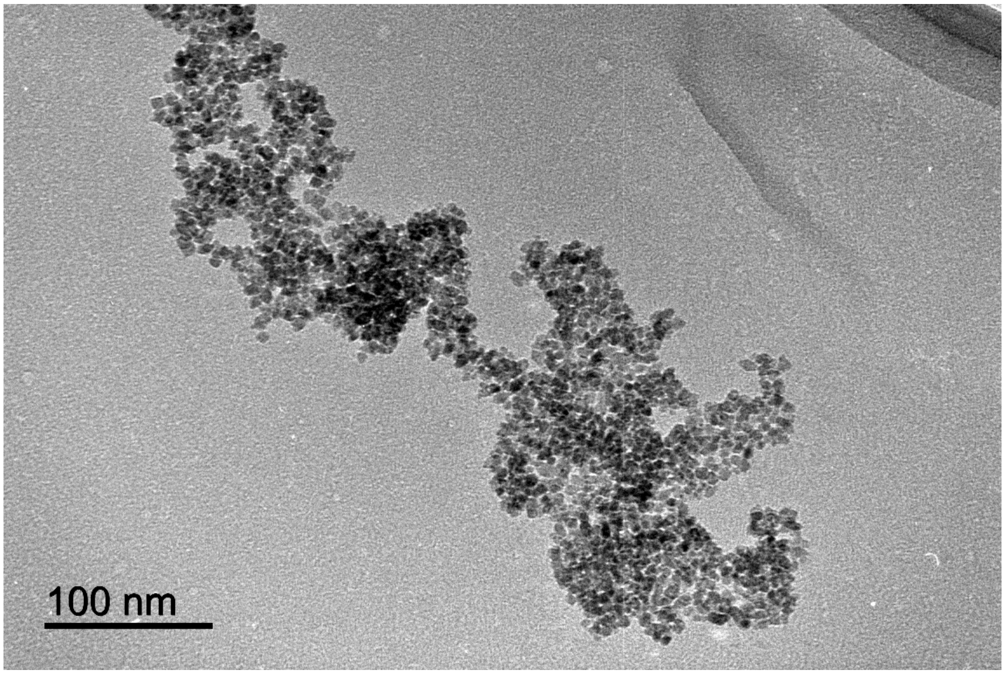

Figure S3. TEM image of iron oxide synthesized in absent of pyrrole.

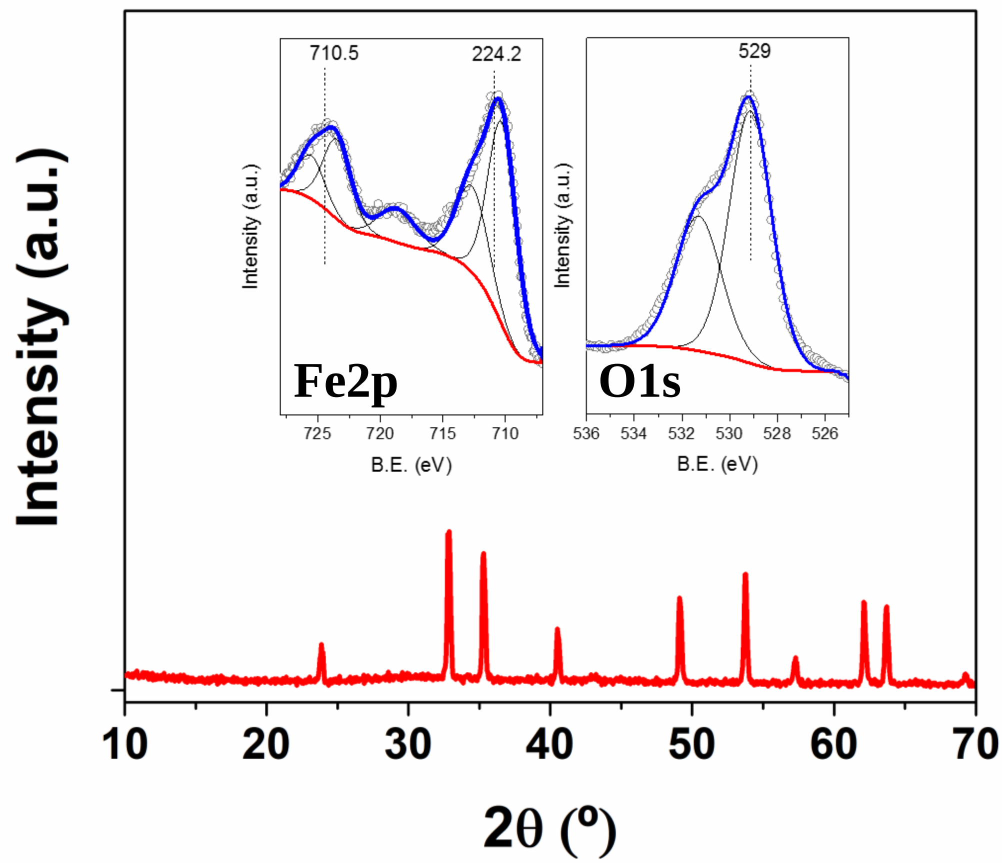

Figure S4. XRD pattern, (Inset) Fe2p and O1s XPS spectra of iron oxide synthesized in absent of pyrrole.

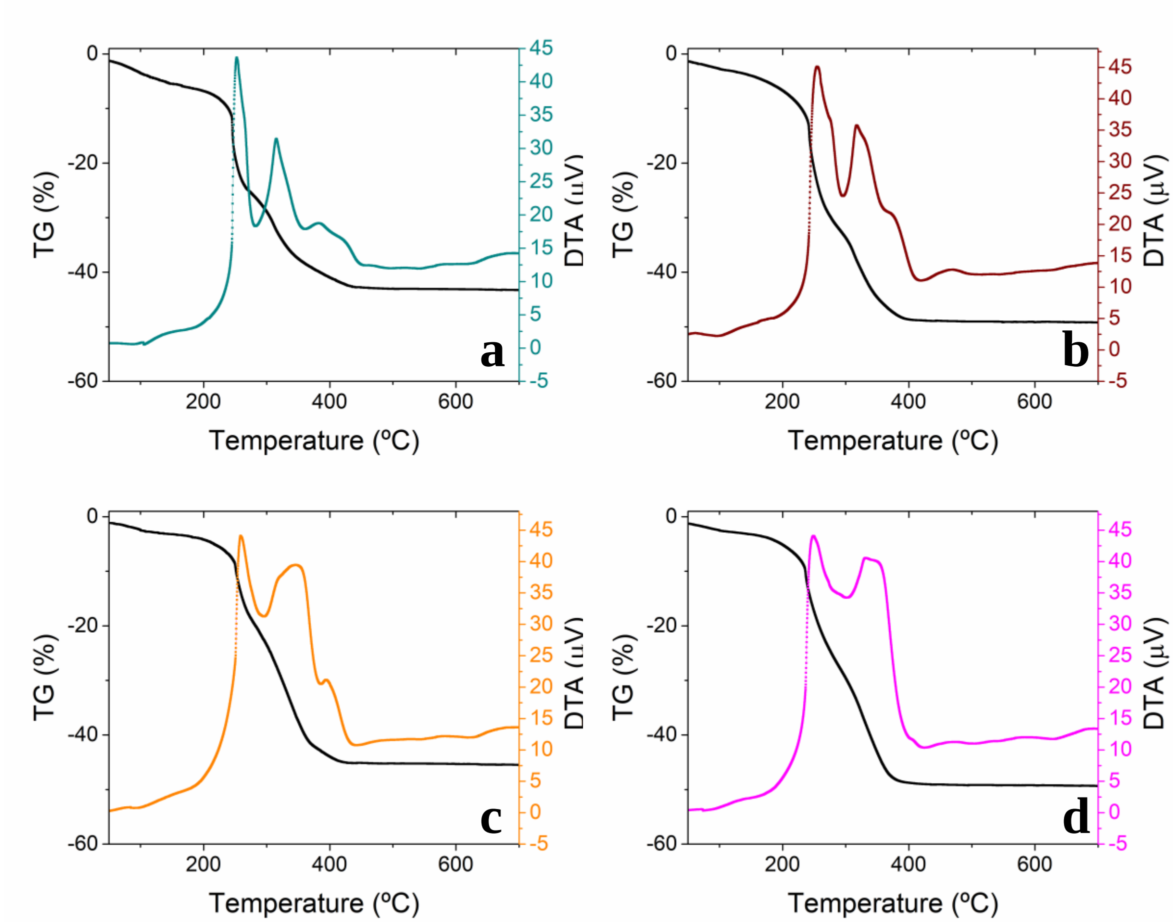

Figure S5. TG and DTA analyses of (a) Ppy@Fe_2O_3-120 °C, (b) Ppy@Fe_2O_3-140 °C, (c) Ppy@Fe_2O_3-160 °C and (d) Ppy@Fe_2O_3-180 °C.

Table S1. XPS data for the PPy@Fe2O3 samples.

Sample	Fe2p3/2 (eV)	O1s (eV)	C1s (eV)	N1s (eV)	C/N	Fe/N	(C+N)/Fe
PP_y@Fe_2O_3 120 °C	710.4	529.7	284.6	399.4	2.8	3.6	1.0
PP_y@Fe_2O_3 140 °C	710.4	529.6	284.5	399.3	3.4	1.7	2.6
PP_y@Fe_2O_3 160 °C	710.2	529.9	2.84.6	399.5	3.6	1.6	3.1
PP_y@Fe_2O_3 180 °C	710.3	529.9	2.84.6	399.4	4.1	1.0	5.0

Table S2. Comparison of the cycling stability of the polypyrrole-modified iron oxide nanostars supercapacitors electrodes with others nanostructured PPy-based supercapacitors.

Device	Electrolyte	Current density/scan rate	Capacitance retention	Ref
V_2O_5-PPy/RGO symmetric	PVA/H_2SO_4	10 A g^{-1}	88.1% (5000 cycles)	1
GF/CNTs/PPy//GF/CNTs/MnO_2	0.5 M Na_2SO_4	1.5 mA cm^{-2}	83.5% (10000 cycles)	2
PPy@MoO_3//AC	0.5 K_2SO_4	0.5 A g^{-1}	83 (600 cycles)	3
PPy-NPG//MnO 2 -NPG	1M $LiClO_4$	100 mV s^{-1}	85% (2000 cycles)	4
PPy@cellulose symmetric	2M NaCl	30 mA cm^{-2}	84% (8500 cycles)	5
PPy-MWCNT symmetric	0.5 Na_2SO_4	20 mA cm^{-2}	94.2% (5000 cycles)	6
FEG/PPy-NS//FEG/MnO_2	3M KCl	6 A g^{-1}	97% (10000 cycles)	7
PPy hydrogel symmetric	PVA/H_2SO_4	-	90% (3000 cycles)	8
CQDs/PPy-NW symmetric	1M KCl	5 mA cm^{-2}	85.2% (5000 cycles)	9
PNTs@$NiCo_2S_4$ symmetric	1M Na_2SO_4	5A g^{-1}	91.6% (4000 cycles)	10
GO/PPy/cellulose	1M NaCl	10 mA cm^{-2}	89.5% (5000 cycles)	11
HDC/$NiCo_2O_4$/PPy	3M NaOH	4A g^{-1}	90% (5000 cycles)	12
nt-GPPy	1M Na_2SO_4	-	95% (1000 cycles)	13
NiNTAs@PPy// MnO_2	PVA/LiCl	100mV s^{-1}	75.3% (10000 cycles)	14
Fe_2O_3@PPy 180	0.5 M Na_2SO_4	40A g^{-1}	97.3% (20000 cycles)	This work

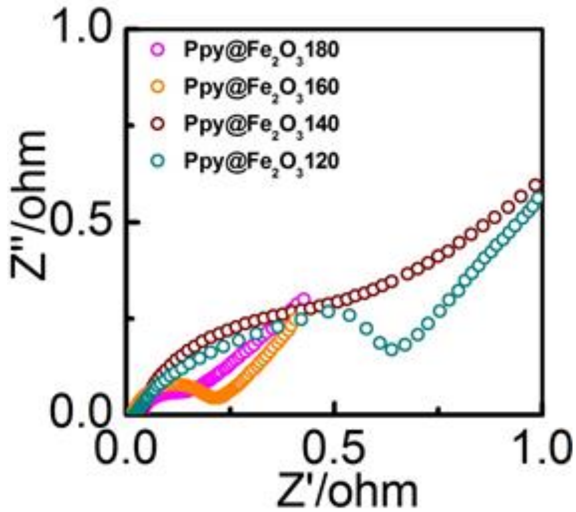

Figure S6. EIS of the four nanohybrids.

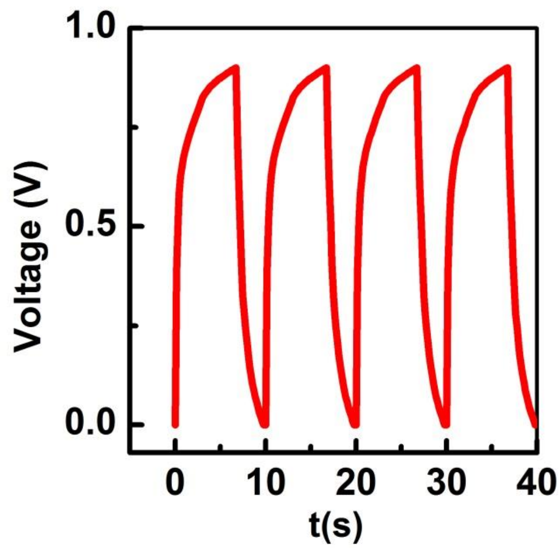

Figure S7. Charge-discharges profiles of the pure Fe_2O_3 nanoparticles. Density current: 25 A g^{-1}.

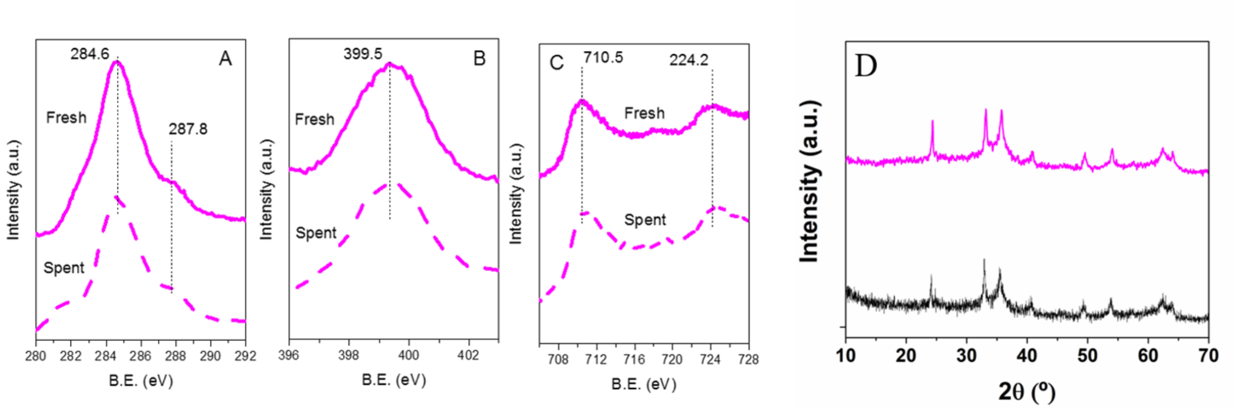

Figure S8, (a) C1s (b) N1s and (c) Fe2p XPS spectra of Ppy@$Fe_2O_3$180 °C sample before and after 20000 cycles. (d) XRD of Ppy@$Fe_2O_3$180 °C sample fresh and after 20000 cycles.

References

(1) Yu, C. F.; Ma, P. P.; Zhou, X.; Wang, A. Q.; Qian, T.; Wu, S. S. and Chen, Q. All-Solid-State Flexible Supercapacitors Based on Highly Dispersed Polypyrrole Nanowire and Reduced Graphene Oxide Composites. *ACS Appl. Mater. Interfaces* **2014**, *6*, 17937.

(2) Liu, J. L.; Zhang, L. L.; Wu, H. B.; Lin, J. Y.; Shen, Z. X; and Lou, X. W.. High-Performance Flexible Asymmetric Supercapacitors based on a New Graphene Foam/Carbon Nanotube Hybrid Film. *Energy Environ. Sci.* **2014**, *7*, 3709.

(3) Liu, Y.; Zhang, B. H.; Yang, Y. Q.; Chang, Z.; Wen, Z. B and Wu, Y. P.. Polypyrrole-Coated α-MoO_3 Nanobelts with Good Electrochemical Performance as Anode Materials for Aqueous Supercapacitors. *J. Mat. Chem. A* **2013**, *1*, 13582.

(4) Hou, Y.; Chen, L. Y.; Liu, P.; Kang, J. L.; Fujita, T. and Chen, M. W. Nanoporous Metal based Flexible Asymmetric Pseudocapacitors. *J. Mat. Chem. A* **2014**, *2*, 10910.

(5) Wang, Z. H.; Tammela,P.; Zhang,P; Stromme, M. and Nyholm,L. High Areal and Volumetric Capacity Sustainable All-Polymer Paper-based Supercapacitors. *J. Mat. Chem. A* **2014**, *2*, 16761.

(6) Zhu, Y. L.; Shi, K. Y. and Zhitomirsky, I. Anionic Dopant–Dispersants for Synthesis of Polypyrrole Coated Carbon Nanotubes and Fabrication of Supercapacitor Electrodes with High Active Mass Loading. *J. Mat. Chem. A* **2014**, *2*, 14666.

(7) Song, Y.; Liu, T. Y.; Xu, X. X.; Feng, D. Y.; Li, Y. and Liu,X. X. Pushing the Cycling Stability Limit of Polypyrrole for Supercapacitors. *Adv. Funct. Mater*. **2015**, *25*, 4626.

(8) Shi, Y.; Pan, L. J.; Liu, B. R.; Wang, Y. Q.; Cui, Y.; Bao, Z. A. and Yu,G. H. Nanostructured Conductive Polypyrrole Hydrogels as High-performance, Flexible Supercapacitor Electrodes. *J. Mat. Chem. A* **2014**, *2*, 6086.

(9) Jian, X.; Li, J. G.; Yang, H. M.; Cao, L. L.; Zhang, E. H. and Liang, Z. H. Carbon Quantum Dots Reinforced Polypyrrole Nanowire Via Electrostatic Self-Assembly Strategy for High-Performance Supercapacitors. *Carbon* **2017**, *114*, 533.

(10) Zhang, J.; Guan, H. J.; Liu, Y.; Zhao, Y. F. and Zhang, B. Hierarchical Polypyrrole Nanotubes@NiCo2S4 Nanosheets Core-Shell Composites with Improved Electrochemical Performance as Supercapacitors. *Electrochim. Acta* **2017**, *258*, 182.

(11) Wan, C. C.; Jiao, Y. and Li, J. Flexible, Highly Conductive, and Free-Standing Reduced Graphene Oxide/Polypyrrole/Cellulose Hybrid Papers for Supercapacitor Electrodes. *J. Mat. Chem. A* **2017**, *5*, 3819.

(12) Xiong, W.; Hu, X.; Wu, X.; Zeng, Y.; Wang, B.; He, G. H. and Zhu, Z. H. A Flexible Fiber-Shaped Supercapacitor Utilizing Hierarchical $NiCo_2O_4$@polypyrrole Core–Shell Nanowires on Hemp-Derived Carbon. *J. Mat. Chem. A* **2015**, *3*, 17209.

(13) Kashani, H.; Chen, L. Y.; Ito, Y.; Han, J. H.; Hirata, A. and Chen, M. W. Bicontinuous Nanotubular Graphene–Polypyrrole Hybrid for High Performance Flexible Supercapacitors. *Nano Energy* **2016**, *19*, 391.

(14) Chen, G. F.; Li, X. X.; Zhang, L. Y.; Li, N.; Ma, T. Y. and Liu,Z. Q. A Porous Perchlorate‐Doped Polypyrrole Nanocoating on Nickel Nanotube Arrays for Stable Wide Potential-Window Supercapacitors. *Adv. Mater.* **2016**, *28*, 7680.