Supporting Information

Encapsulation of Fe_3O_4 between Copper Nanorod and Thin TiO_2 Film by ALD for Lithium-Ion Capacitors

Yuzhu Li, Tian Liang, Rui Wang, Beibei He, Yansheng Gong, Huanwen Wang*

Engineering Research Center of Nano-Geomaterials of Ministry of Education, Faculty of Material and Chemistry, China University of Geosciences, Wuhan 430074, China.
E-mail: wanghw@cug.edu.cn

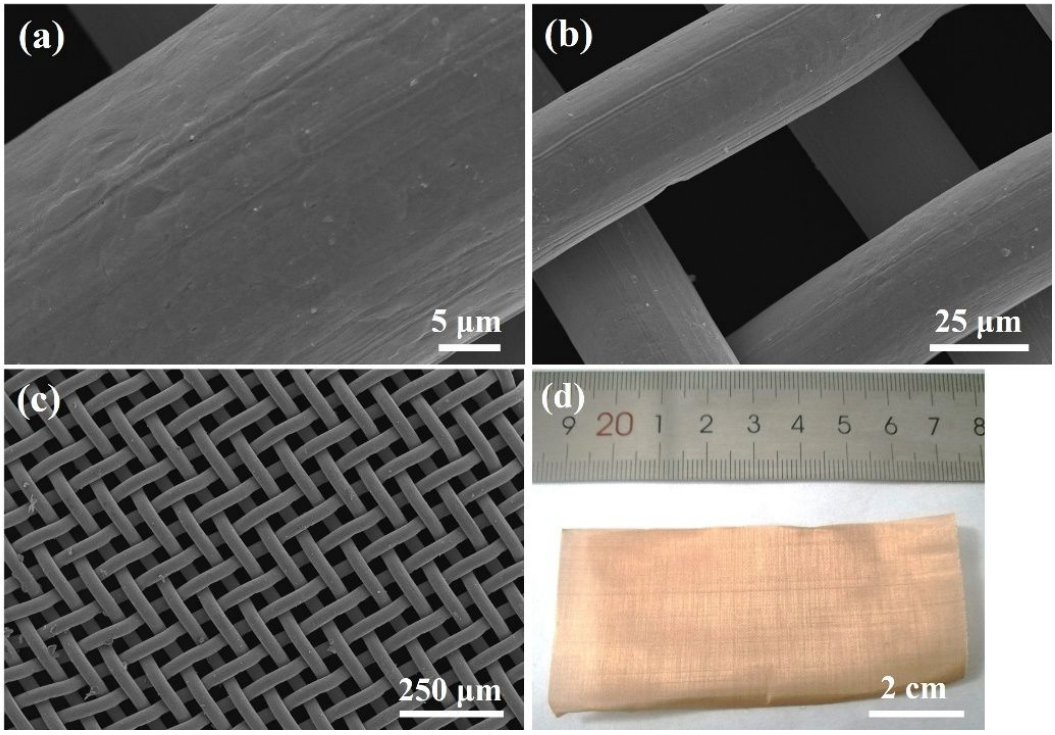

Figure S1. (a-c) SEM images and (d) Photographs of Cu screen.

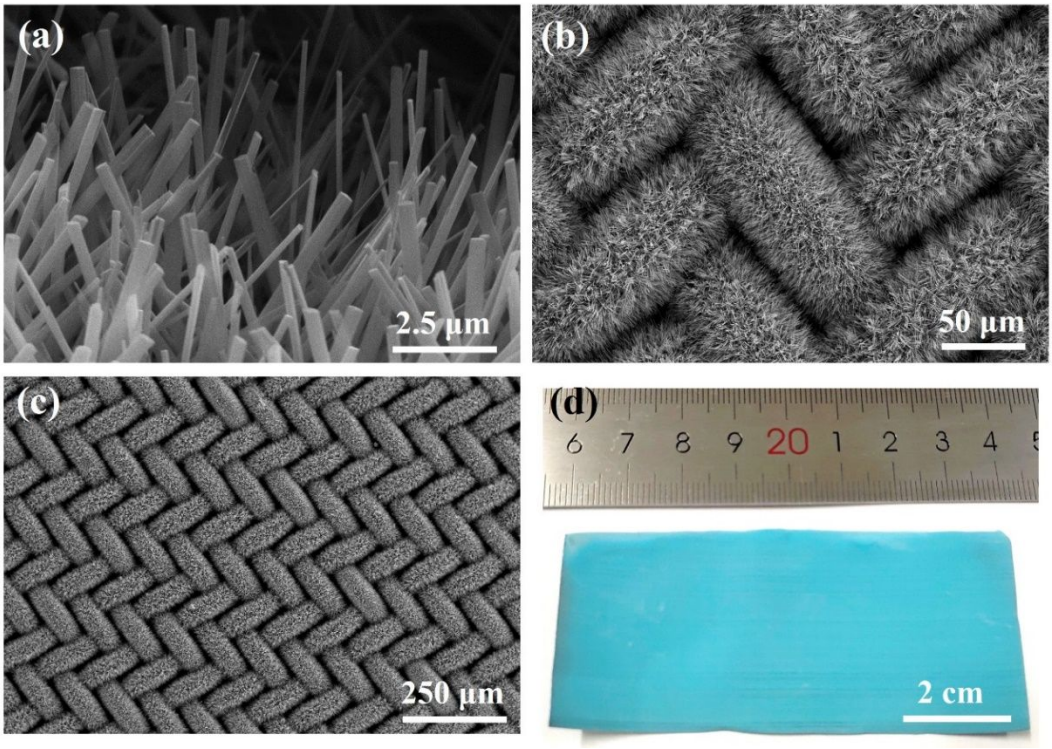

Figure S2. (a-c) SEM images and (d) Photographs of Cu@$Cu(OH)_2$.

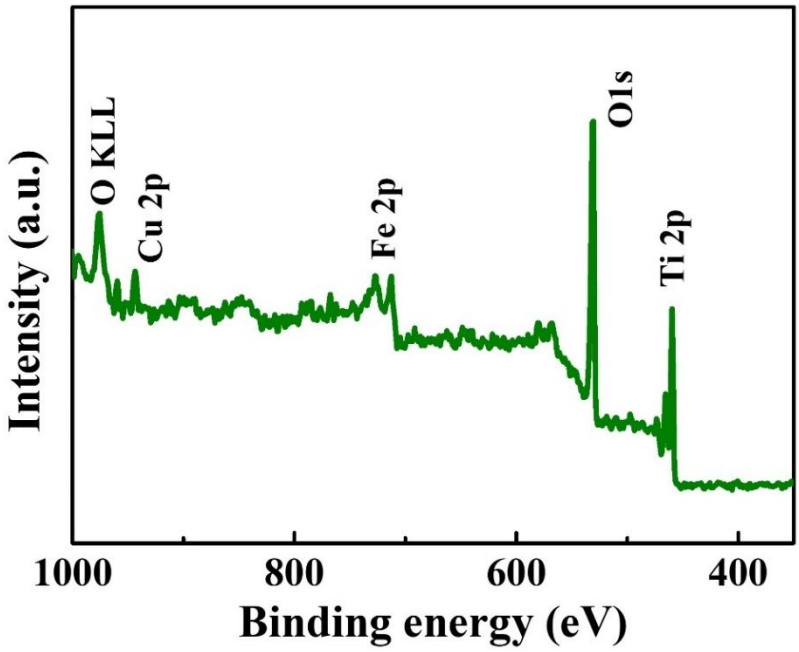

Figure S3. XPS spectrum Cu@Fe_3O_4ЭTiO_2.

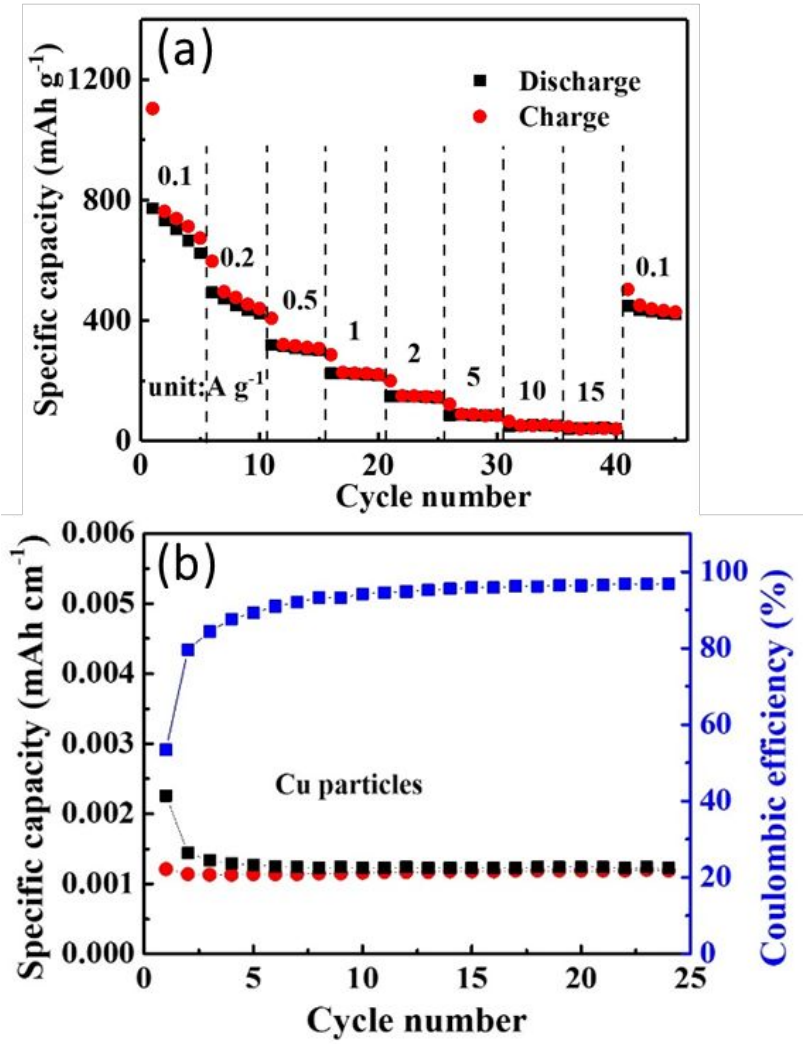

Figure S4. (a) Rate performances of Cu@commercial Fe_3O_4 powder electrodes and (b) the Li-storage performance of copper grid/Cu nanorods electrodes at 0.14 mA cm^{-2}.

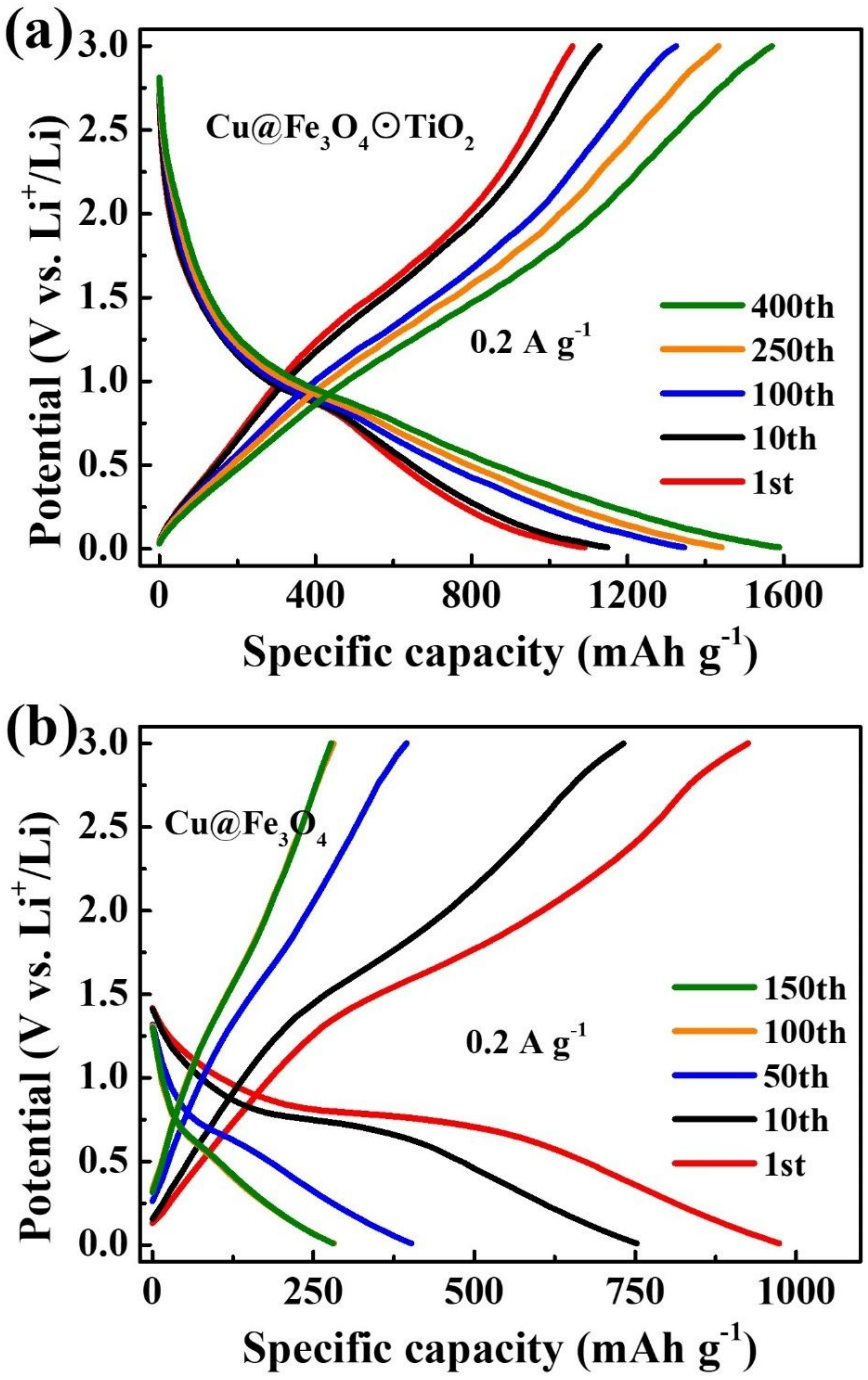

Figure S5. The corresponding GCD profiles of (a) $Cu@Fe_3O_4ƆTiO_2$ and (b) $Cu@Fe_3O_4$ and at 0.2 A g^{-1}.

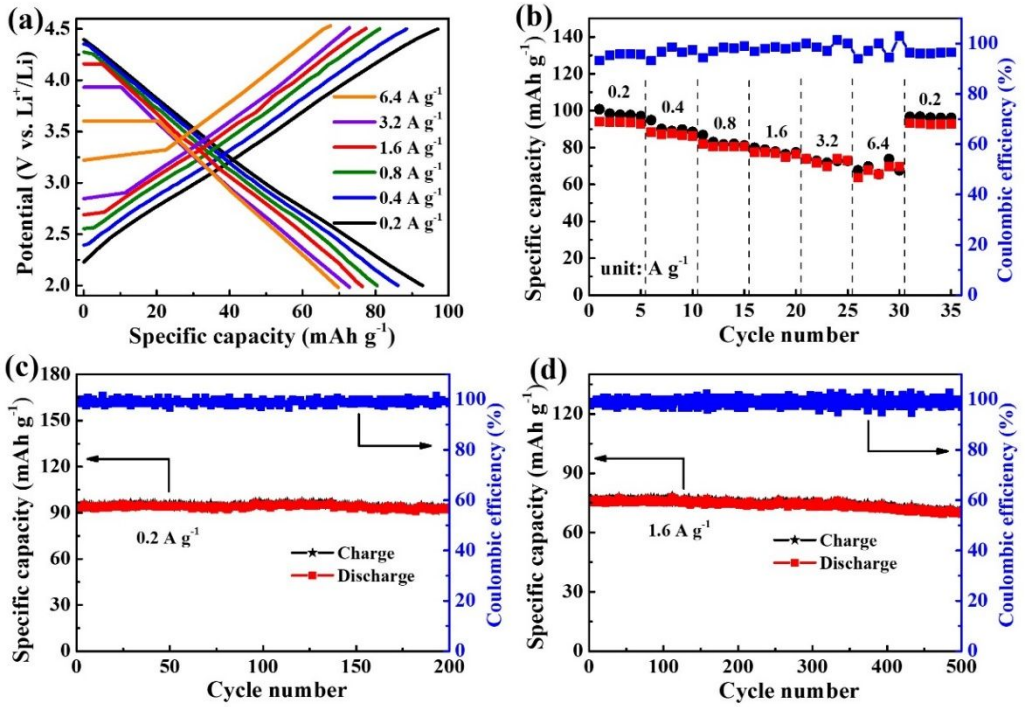

Figure S6. The electrochemical performances of commercial AC cathode within the potential widow of 2.0-4.5 V (vs. Li/Li^+).

Table S1. Comparison of cycle performance and rate performance for Fe_3O_4-base anodes reported previously.

Materials	Voltage Range (V)	Cycle performance		Rate performance		Ref.
		Capacity ($mAhg^{-1}$) /cycles	Current density($A \cdot g^{-1}$)	Capacity ($mAhg^{-1}$)	Current density ($A \cdot g^{-1}$)	
Fe_3O_4@C-3	0.005-3	1246/300	0.8	1293, 1167, 1108, 952, 822, 681, 461	0.4, 0.8, 1, 2, 3, 5, 10	1
		990/300	2			
		520/1000	5			
Fe_3O_4@PCM/ graphene	0.01-3	1077/100	0.18	760 ,665, 510 ,407	0.9, 1.8, 4.6, 9.2	2
Fe_3O_4@C	0-3	833.5/350	0.5	1116.1, 1054.1, 906.7, 762.4, 587.2, 323.1	0.1, 0.2, 0.5, 1, 2, 5	3
Fe_3O_4@C/RGO	0.005-3	1278/100	0.1	972, 943, 831, 694, 518	0.1, 0.2, 0.5, 1, 2	4
		789/100	1			
Fe_3O_4@N-C	0.01-3	1204.3/100	0.5	1206.3, 1053.1, 940.6, 750.0, 609.4, 496.9, 412.5	0.5, 1, 2, 5, 10, 15, 20	5
		1063/1000	1			
Fe_3O_4 dots/3DHC	0.01-3	1082/200	0.3	1078, 963, 731,	0.5, 1, 3	6
Fe_3O_4@C-2	0.01-3	900/2000	5	1012, 890, 800, 695, 575, 477, 370	0.1, 0.5, 1, 2, 5, 10, 20	7
		470/8000	10			
hierarchical Fe_3O_4 hollow spheres	0.01-3	1046/100	0.5	992, 853, 716, 548, 457	1, 2, 4, 8, 10	8
Fe_3O_4/C	0.01-3	837/200	0.5	990, 933, 846, 743, 648, 453	0.3, 0.5, 1, 2, 3, 5	9
FeO_x@C	0.001-3	790/100	0.2	820, ~700, ~580, ~480, ~370	0.2, 0.5, 1, 2, 4	10
Fe_3O_4@GS/GF	0.01-3	1059/150	0.093	856.8, ~750, ~670, ~600,	0.15, 0.3, 0.6, 1.2, 2.4,	11

				~490, 363	4.8	
rGO@Fe_3O_4	0.01-3	675/80	0.1	725, 709, 618, 523, 424, 300, 218	0.1, 0.2, 0.5, 1, 2, 5, 10	12
		649/150	0.25			
Cu@Fe_3O_4ƏTiO_2	0.01-3	1580/400	0.2	908, 1061, 982, 923, 808, 713, 598, 489	0.1, 0.2, 0.5, 1, 2, 5, 10, 15	This work
		831/1000	2			

Table S2 Energy and power density comparison with the reports in the literature for hybrid LIC devices.

Positive electrode	Negative electrode	Voltage Window (V)	Energy density (Wh kg^{-1})	Corresponding Power density (W kg^{-1})	Ref.
PF16	FRGO	0-4	148.3	141	13
			71.5	7800	
APDC	VN-RGO	0-4	162	200	14
			64	10, 000	
HDMPC	HDMPC	0-4	106.4	500	15
			10.2	88, 800	
AC	Fe_3O_4–G	1-4	120	130	16
			60.5	45, 400	
AC	TiO_2-rGO	1-3	42	800	17
			8.9	8000	
CFs	$TiNb_2O_7$@C	0.8-3.2	110.4	99.58	18
			20	5464	
AC	Fe_3O_4@C	0-4	110.1	250	3
			36.8	2500	
AC	MA@PVDF	0-4.3	158.7	107.5	19
			70.9	10750	
AC	$Co_xFe_yO_z$@rGO	1-4	120	100	20
			43	2500	
ACN	L-Nb_2O_5 NWs/rGO	1-4	106	580	21
			32	14000	
a-EW-NaCl	Fe_3O_4@C	1-4	124.7	2547	22
			57.8	16984	
NHCN-2	SHSG	2-4.5	146	650	23
			103	52000	
PdCS	AMC	0.5-4	133	210	24
			42	11200	
AC	$Ti_3C_2T_x$/CNT	1-4	67	258	25
			19	5797	
PRGO	$BiVO_4$	0.01-4	152	384	26
			42	3861	
CMK-3	hp-LVO/C	0.2-4.3	105	188	27
			62	9300	
MPC	Co_3ZnC@NC	1-4.5	141.4	275	28
			15.2	10300	
PSC	B-Si/SiO_2/C	2-4.5	128	1229	29
			89	9704	
AC	Cu@Fe_3O_4ↃTiO_2	0-4	154.8	200	This work
			66.2	30000	

REFERENCES

(1) Han, D.; Guo, G.; Yan, Y.; Li, T.; Wang, B.; Dong, A. Pomegranate-Like, Carbon-Coated Fe_3O_4 Nanoparticle Superparticles for High-Performance Lithium Storage. *Energy Storage Mater.* **2018,** *10*, 32-39.

(2) Hao, S.; Zhang, B.; Wang, Y.; Li, C.; Feng, J.; Ball, S.; Srinivasan, M.; Wu, J.; Huang, Y. Hierarchical Three-dimensional Fe_3O_4@porous Carbon Matrix/Graphene Anodes for High Performance Lithium Ion Batteries. *Electrochim. Acta* **2018,** *260*, 965-973.

(3) Han, C.; Xu, L.; Li, H.; Shi, R.; Zhang, T.; Li, J.; Wong, C. P.; Kang, F.; Lin, Z.; Li, B. Biopolymer-Assisted Synthesis of 3D Interconnected Fe_3O_4@Carbon Core@Shell as Anode for Asymmetric Lithium Ion Capacitors. *Carbon* **2018,** *140*, 296-305.

(4) Hao, S. M.; Li, Q. J.; Qu, J.; An, F.; Zhang, Y. J.; Yu, Z. Z. Neuron-Inspired Fe_3O_4/Conductive Carbon Filament Network for High-Speed and Stable Lithium Storage. *ACS Appl. Mater. Interfaces* **2018,** *10*, 17923-17932.

(5) Liu, B.; Zhang, Q.; Jin, Z.; Zhang, L.; Li, L.; Gao, Z.; Wang, C.; Xie, H.; Su, Z. Uniform Pomegranate-Like Nanoclusters Organized by Ultrafine Transition Metal Oxide@Nitrogen-Doped Carbon Subunits with Enhanced Lithium Storage Properties. *Adv. Energy Mater.* **2017,** *8*, 1702347.

(6) Li, C.; Li, L.; Li, Z.; Zhong, W.; Li, Z.; Yang, X.; Zhang, G.; Zhang, H. Fabrication of Fe_3O_4 Dots Embedded in 3D Honeycomb-Like Carbon Based on Metallo-Organic Molecule with Superior Lithium Storage Performance. *Small* **2017,** *13*, 1701351.

(7) Liu, Z.; Yu, X. Y.; Paik, U. Etching-in-a-Box: A Novel Strategy to Synthesize Unique Yolk-Shelled Fe_3O_4@Carbon with an Ultralong Cycling Life for Lithium Storage. *Adv. Energy Mater.* **2016,** *6*, 1502318.

(8) Ma, F. X.; Hu, H.; Wu, H. B.; Xu, C. Y.; Xu, Z.; Zhen, L.; David Lou, X. W. Formation of Uniform Fe_3O_4 Hollow Spheres Organized by Ultrathin Nanosheets and Their Excellent Lithium Storage Properties. *Adv. Mater.* **2015,** *27*, 4097-4101.

(9) Ma, F. X.; Wu, H. B.; Xu, C. Y.; Zhen, L.; Lou, X. W. Self-Organized Sheaf-Like Fe_3O_4/C Hierarchical Microrods with Superior Lithium Storage Properties. *Nanoscale* **2015,** *7*, 4411-4414.

(10) Zhang, H.; Zhou, L.; Noonan, O.; Martin, D. J.; Whittaker, A. K.; Yu, C. Tailoring the Void Size of Iron Oxide@Carbon Yolk-Shell Structure for Optimized Lithium Storage. *Adv. Funct. Mater.* **2014,** *24*, 4337-4342.

(11) Wei, W.; Yang, S.; Zhou, H.; Lieberwirth, I.; Feng, X.; Mullen, K. 3D Graphene Foams Cross-Linked with Pre-Encapsulated Fe_3O_4 Nanospheres for Enhanced Lithium Storage. *Adv. Mater.* **2013,** *25*, 2909-2914.

(12) Liang, T.; Wang, H.; Xu, D.; Liao, K.; Wang, R.; He, B.; Gong, Y.; Yan, C. High-Energy Flexible Quasi-Solid-State Lithium-Ion Capacitors Enabled by A Freestanding rGO-Encapsulated Fe_3O_4 Nanocube Anode and A Holey rGO Film Cathode. *Nanoscale* **2018,** *10*, 17814-17823.

(13) Zhang, T.; Zhang, F.; Zhang, L.; Lu, Y.; Zhang, Y.; Yang, X.; Ma, Y.; Huang, Y. High Energy Density Li-Ion Capacitor Assembled with All Graphene-Based Electrodes. *Carbon* **2015,** *92*, 106-118.

(14) Wang, R.; Lang, J.; Zhang, P.; Lin, Z.; Yan, X. Fast and Large Lithium Storage in 3D Porous VN Nanowires-Graphene Composite as a Superior Anode Toward High-Performance Hybrid Supercapacitors. *Adv. Funct. Mater.* **2015,** *25*, 2270-2278.

(15) Niu, J.; Shao, R.; Liu, M.; Liang, J.; Zhang, Z.; Dou, M.; Huang, Y.; Wang, F. Porous Carbon Electrodes with Battery-Capacitive Storage Features for High Performance Li-Ion Capacitors. *Energy Storage Mater.* **2018,** *12*, 145-152.

(16) Zhang, S.; Li, C.; Zhang, X.; Sun, X.; Wang, K.; Ma, Y. High Performance Lithium-Ion Hybrid Capacitors Employing Fe_3O_4-Graphene Composite Anode and Activated Carbon Cathode. *ACS Appl. Mater. Interfaces* **2017,** *9*, 17136-17144.
(17) Kim, H.; Cho, M. Y.; Kim, M. H.; Park, K. Y.; Gwon, H.; Lee, Y.; Roh, K. C.; Kang, K. A Novel High-Energy Hybrid Supercapacitor with an Anatase TiO_2-Reduced Graphene Oxide Anode and an Activated Carbon Cathode. *Adv. Energy Mater.* **2013,** *3*, 1500-1506.
(18) Wang, X.; Shen, G. Intercalation Pseudo-Capacitive $TiNb_2O_7$@Carbon Electrode for High-Performance Lithium Ion Hybrid Electrochemical Supercapacitors with Ultrahigh Energy Density. *Nano Energy* **2015,** *15*, 104-115.
(19) Hu, Z.; Sayed, S.; Jiang, T.; Zhu, X.; Lu, C.; Wang, G.; Sun, J.; Rashid, A.; Yan, C.; Zhang, L.; Liu, Z. Self-Assembled Binary Organic Granules with Multiple Lithium Uptake Mechanisms toward High-Energy Flexible Lithium-Ion Hybrid Supercapacitors. *Adv. Energy Mater.* **2018,** *8*, 1802273.
(20) Huang, H.; Wang, X.; Tervoort, E.; Zeng, G.; Liu, T.; Chen, X.; Sologubenko, A.; Niederberger, M. Nano-Sized Structurally Disordered Metal Oxide Composite Aerogels as High-Power Anodes in Hybrid Supercapacitors. *ACS Nano* **2018,** *12*, 2753-2763.
(21) Song, H.; Fu, J.; Ding, K.; Huang, C.; Wu, K.; Zhang, X.; Gao, B.; Huo, K.; Peng, X.; Chu, P. K. Flexible Nb_2O_5 Nanowires/Graphene Film Electrode for High-Performance Hybrid Li-Ion Supercapacitors. *J. Power Sources* **2016,** *328*, 599-606.
(22) Shi, R.; Han, C.; Li, H.; Xu, L.; Zhang, T.; Li, J.; Lin, Z.; Wong, C. P.; Kang, F.; Li, B. NaCl-Templated Synthesis of Hierarchical Porous Carbon with Extremely Large Specific Surface Area and Improved Graphitization Degree for High Energy Density Lithium Ion Capacitors. *J. Mater. Chem. A* **2018,** *6*, 17057-17066.
(23) Li, C.; Zhang, X.; Wang, K.; Sun, X.; Ma, Y. High-Power and Long-Life Lithium-Ion Capacitors Constructed from N-Doped Hierarchical Carbon Nanolayer Cathode and Mesoporous Graphene Anode. *Carbon* **2018,** *140*, 237-248.
(24) Lee, W. S. V.; Huang, X.; Tan, T. L.; Xue, J. M. Low Li(+) Insertion Barrier Carbon for High Energy Efficient Lithium-Ion Capacitor. *ACS Appl. Mater. Interfaces* **2018,** *10*, 1690-1700.
(25) Yu, P.; Cao, G.; Yi, S.; Zhang, X.; Li, C.; Sun, X.; Wang, K.; Ma, Y. Binder-Free 2D Titanium Carbide (Mxene)/Carbon Nanotube Composites for High-Performance Lithium-Ion Capacitors. *Nanoscale* **2018,** *10*, 5906-5913.
(26) Dubal, D. P.; Jayaramulu, K.; Zboril, R.; Fischer, R. A.; Gomez-Romero, P. Unveiling $BiVO_4$ Nanorods as A Novel Anode Material for High Performance Lithium Ion Capacitors: Beyond Intercalation Strategies. *J. Mater. Chem. A* **2018,** *6*, 6096-6106.
(27) Xu, X.; Niu, F.; Zhang, D.; Chu, C.; Wang, C.; Yang, J.; Qian, Y. Hierarchically Porous Li_3VO_4/C Nanocomposite as An Advanced Anode Material for High-Performance Lithium-Ion Capacitors. *J. Power Sources* **2018,** *384*, 240-248.
(28) Zhu, G.; Chen, T.; Wang, L.; Ma, L.; Hu, Y.; Chen, R.; Wang, Y.; Wang, C.; Yan, W.; Tie, Z.; Liu, J.; Jin, Z. High Energy Density Hybrid Lithium-Ion Capacitor Enabled by Co_3ZnC@N-Doped Carbon Nanopolyhedra Anode and Microporous Carbon Cathode. *Energy Storage Mater.* **2018,** *14*, 246-252.
(29) Yi, R.; Chen, S.; Song, J.; Gordin, M. L.; Manivannan, A.; Wang, D. High-Performance Hybrid Supercapacitor Enabled by A High-Rate Si-based Anode. *Adv. Funct. Mater.* **2014,** *24*, 7433-7439.