Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Hierarchical $V_4C_3T_X$@NiO-reduced graphene oxide heterostructure hydrogel and defective reduced graphene oxide hydrogel as free-standing anode and cathode for high-performance asymmetric supercapacitor

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Table S1. Comparison of specific capacitance of $Ti_3C_2T_X$-based heterostructured electrodes.

Materials	Electrolyte	Specific capacitance	Current density or Scan rate	Ref.
$Ti_3C_2T_X$/CNF/PC	1 M KOH	143 mF cm^{-2}	0.1 mA cm^{-2}	[1]
N,O co-doped C@$Ti_3C_2T_X$	6 M KOH	250.6 F g^{-1}	1 A g^{-1}	[2]
$Ti_3C_2T_X$/ZIF-67/CoV_2O_6	1 M KOH	285.5 F g^{-1}	1 A g^{-1}	[3]
1T-MoS_2/$Ti_3C_2T_X$	1 M H_2SO_4	386.7 F g^{-1}	1 A g^{-1}	[4]
MnO_2/$Ti_3C_2T_X$/CC	1 M LiCl	411.5 F g^{-1}	1 A g^{-1}	[5]
PPy/$Ti_3C_2T_X$	1 M H_2SO_4	458 F g^{-1}	2 mV s^{-1}	[6]
$Ti_3C_2T_X$@PDA/$NiCo_2S_4$	3 M KOH	495 F g^{-1}	2 mV s^{-1}	[7]
400-KOH-$Ti_3C_2T_X$	1 M H_2SO_4	517 F g^{-1}	1 A g^{-1}	[8]
$Ti_3C_2T_X$/NF	6 M KOH	654 F g^{-1}	1 A g^{-1}	[9]
MXene/rGO	3 M H_2SO_4	1040 F cm^{-3}	2 mV s^{-1}	[10]
Co_2NiO_4/$Ti_3C_2T_X$	3 M KOH	719.5 F g^{-1}	0.5 A g^{-1}	[11]
Ti_3C_2/Ni-Co-Al-LDH	1 M KOH	748.2 F g^{-1}	1 A g^{-1}	[12]
$Ti_3C_2T_X$@NiO-RGO	1 M KOH	966 F g^{-1}	1 A g^{-1}	[13]
$V_4C_3T_X$@NiO-RGO	1 M KOH	1014.5 F g^{-1}	1 A g^{-1}	This work

Table S2 Comparison of specific capacitance for various carbon materials in aqueous electrolytes reported in the literature.

Material	Electrolyte	Specific capacitance (F g^{-1})	Current density (A g^{-1})	Ref.
NG-900	6 M KOH	130	0.5	[14]
aNG	1 M KOH	132.4	0.1	[15]
TsG	6 M KOH	180	0.5	[16]
$AC800NH_3$	6 M KOH	196	1	[17]
LSG	1 M H_3PO_4	202	1	[18]
HPCFs	6 M KOH	206	1	[19]
C-900	6 M KOH	210	1	[20]
PANecoal-AC_5	6 M KOH	230	1	[21]
AC800	7 M KOH	232	0.05	[22]
N-HPCs	6 M KOH	335	0.1	[23]
PCPs	1 M KOH	245	1	[24]
DRGO	1 M KOH	258	1	This work

References

[1] Chen, W. M.; Zhang, D. T.; Yang, K.; Luo, M.; Yang, P.; Zhou, X. Y. MXene ($Ti_3C_2T_X$)/cellulose nanofiber/porous carbon film as free-standing electrode for ultrathin and flexible supercapacitors. *Chemical Engineering Journal*. **2021**, 413, 127524.

[2] Pan, Z. H.; Ji, X. H. Facile synthesis of nitrogen and oxygen co-doped C@Ti_3C_2 MXene for high performance symmetric supercapacitors. *Journal of Power Sources*. **2019**, 439, 227068.

[3] Liu, C. L.; Bai, Y.; Li, W. T.; Yang, F. Y.; Zhang, G. X.; Pang, H. In Situ Growth of Three-Dimensional MXene/Metal–Organic Framework Composites for High-Performance Supercapacitors. *Angew Chem Int Ed Engl*. **2022**, 61, e202116282.

[4] Wang, X.; Li, H.; Li, H.; Lin, S.; Ding, W.; Zhu, X. G.; Sheng, Z. G.; Wang, H.; Zhu, X. B.; Sun, Y. P. 2D/2D 1T-MoS_2/Ti_3C_2 MXene Heterostructure with Excellent Supercapacitor Performance. *Advanced Functional Materials*. **2020**, 30, 0190302.

[5] Chen, X. H.; Liu, Y.; Zhou, Q.; Su, F. H. Facile Synthesis of MnO_2/$Ti_3C_2T_X$/CC as Positive Electrode of All-Solid-State Flexible Asymmetric Supercapacitor. *ChemistrySelect*. **2020**, 5, 14768-14775.

[6] Wei, D.; Wu, W. L.; Zhu, J. F.; Wang, C. W.; Zhao, C. H.; Wang, L. A facile strategy of polypyrrole nanospheres grown on Ti_3C_2-MXene nanosheets as advanced supercapacitor electrodes. *Journal of Electroanalytical Chemistry*. **2020**, 877, 114538.

[7] Wu, W. L.; Niu, D. J.; Zhu, J. F.; Gao, Y.; Wei, D.; Zhao, C. H.; Wang, C. W.; Wang, F.; Wang, L.;Yang, L. Q. Hierarchical architecture of Ti_3C_2@PDA/$NiCo_2S_4$ composite electrode as high-performance supercapacitors. *Ceramics International*. **2019**, 45, 16261-16269.

[8] Li, J.; Yuan, X. T.; Lin, C.; Yang, Y. Q.; Xu, L.; Du, X.; Xie, J. L.; Lin, J. H.; Sun, J. L. Achieving High Pseudocapacitance of 2D Titanium Carbide (MXene) by Cation Intercalation and Surface Modification. *Advanced Energy Materials*. **2017**, 7, 1-6.

[9] Guo, J.; Zhao, Y. Y.; liu, A. N.; Ma, T. L. Electrostatic self-assembly of 2D delaminated MXene (Ti_3C_2) onto Ni foam with superior electrochemical performance for supercapacitor. *Electrochimica Acta*. **2019**, 305, 164-174.

[9] Yan, J.; Ren, C. E.; Maleski, K.; Hatter, C. B.; Anasori, B.; Urbankowski, P.; Sarycheva, A.; Gogotsi, Y. Flexible MXene/Graphene Films for Ultrafast Supercapacitors with Outstanding Volumetric Capacitance. *Advanced Functional Materials*. **2017**, 27, 1701264.

[10] Song, J. R.; Hu, P. F.; Liu, Y.; Song, W. X.; Wu, X. Enhanced Electrochemical Performance of Co_2NiO_4/$Ti_3C_2T_X$ Structures through Coupled Synergistic Effects. *ChemistrySelect*. **2019**, 4, 12886-12890.

[11] Zhao, R. Z.; Wang, M. Q.; Zhao, D. Y.; Li, H.; Wang, C. X.; Yin, L. W. Molecular-Level Heterostructures Assembled from Titanium Carbide MXene and Ni-Co-Al Layered Double Hydroxide Nanosheets for All-solid-state Flexible Asymmetric High-Energy Supercapacitors. *ACS Energy Letters*. **2017**, 3, 132-140.

[12] Chen, W. W.; Peng, Y.; Qiu, Z. H.; Zhang, X.; Xu, H. J. 3D hierarchical $Ti_3C_2T_X$@NiO-reduced graphene oxide heterostructure hydrogel as free-standing electrodes for high performance supercapacitor. *Journal of Alloys and Compounds*. **2022**, 901, 163614.

[13] Lee, K. H.; Oh, J.; Son, J. G.; Kim, H.; Lee, S. S. Nitrogen-Doped Graphene Nanosheets from Bulk Graphite using Microwave Irradiation. *ACS Appl Mater Interfaces*. **2014**, 6, 6361-6368.

[14] Zheng, B.; Chen, T. W.; Xiao, F. N.; Bao, W. J.; Xia, X. H. KOH-activated nitrogen-doped graphene by means of thermal annealing for supercapacitor. *Journal of Solid State Electrochemistry*. **2013**, 17, 1809-1814.

[15] Wen, P.; Gong, P. W.; Mi, Y. J.; Wang, J. Q.; Yang, S. R. Scalable fabrication of high quality graphene by exfoliation of edge sulfonated graphite for supercapacitor application. *RSC Advances*. **2014**, 4, 35914-35918.

[16] Benedetti, M.; Girelli, C. R.; Antonucci, D.; De Pascali, S. A.; Fanizzi, F. P. New method for the synthesis of [PtCl{η^1-$CH_2C(O)R$}(N-N)] ketonyl derivatives starting from the Zeise's salt. *Inorganica Chimica Acta*. **2014**, 413, 109-114.

[17] Guo, J. R.; Xu, X. T.; Hill, J. P.; Wang, L. P.; Dang, J. J.; Kang, Y. Q.; Li, Y. L.; Guan, Y. S.; Yamauchi, Y. Graphene–carbon 2D heterostructures with hierarchically-porous P, N-doped layered architecture for capacitive deionization. *Chem Sci*. **2021**,12,10334-10340.

[18] Lv, Y.; Gan, L. H.; Liu, M. X.; Xiong, W.; Xu, Z. J.; Zhu, D. Z.; Wright, D. S. A self-template synthesis of hierarchical porous carbon foams based on banana peel for supercapacitor electrodes. *Journal of Power Sources*. **2012**, 209, 152-157.

[19] Qiu, B.; Pan, C. T.; Qian, W. J.; Peng, Y. J.; Qiu, L. H.; Yan, F. Nitrogen-doped mesoporous carbons originated from ionic liquids as electrode materials for supercapacitors. *Journal of Materials Chemistry A*. **2013**, 1, 6373-6378.

[20] Zhao, H. Y.; Wang, L. X.; Jia, D. Z.; Xia, W.; Li, J.; Guo, Z. P. Coal based activated carbon nanofibers prepared by electrospinning. *J. Mater. Chem. A*. **2014**, 2, 9338-9344.

[21] Shang, T. X.; Zhang, M. Y.; Jin, X. J. Easy procedure to prepare nitrogen-containing activated carbons for supercapacitors. *RSC Adv.* **2014**, 4, 39037-39044.

[22] Yang, X. W.; Zhuang, X. D.; Huang, Y. J.; Jiang, J. Z.; Tian, H.; Wu, D. Q.; Zhang, F.; Mai, Y. Y.; Feng, X. L. Nitrogen-Enriched Hierarchically Porous Carbons Fabricated by Graphene Aerogel Templated Schiff-base Chemistry for High Performance Electrochemical Capacitors. *Polymer Chemistry*. **2015**, 6, 1088-1095.

[23] Yi, H.; Wang, H. W.; Jing, Y. T.; Peng, T. Q.; Wang, X. F. Asymmetric supercapacitors based on carbon nanotubes@NiO ultrathin nanosheets core-shell composites and MOF-derived porous carbon polyhedrons with super-long cycle life. Journal of Power Sources. 2015, 285, 281-290.