Supplementary Information

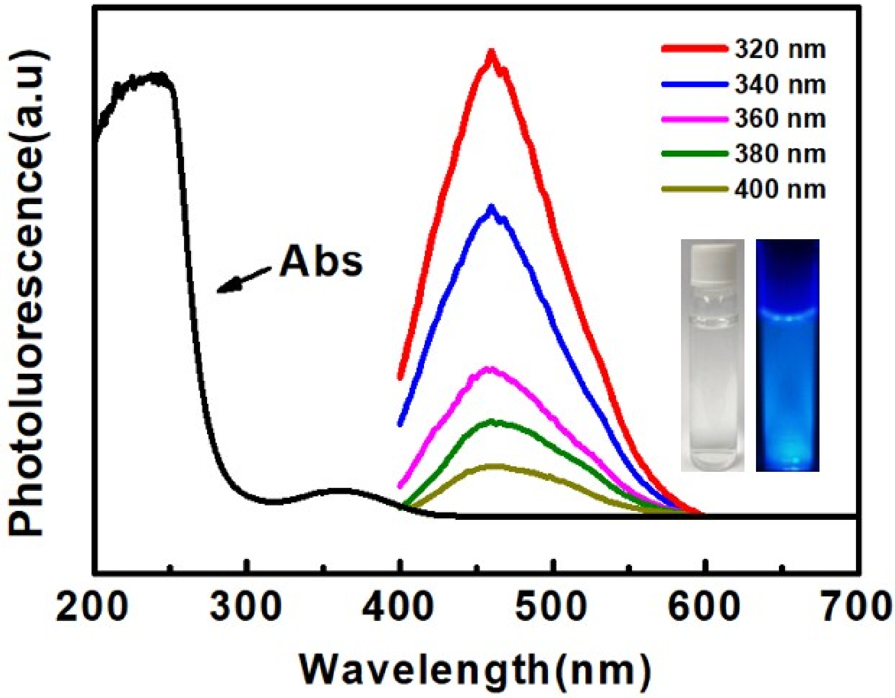

Figure S1. UV-vis absorption and PL emission spectra of prepared GQDs in water solution. Optical photograph obtained under natural light (left) and UV light (365 nm,right)..

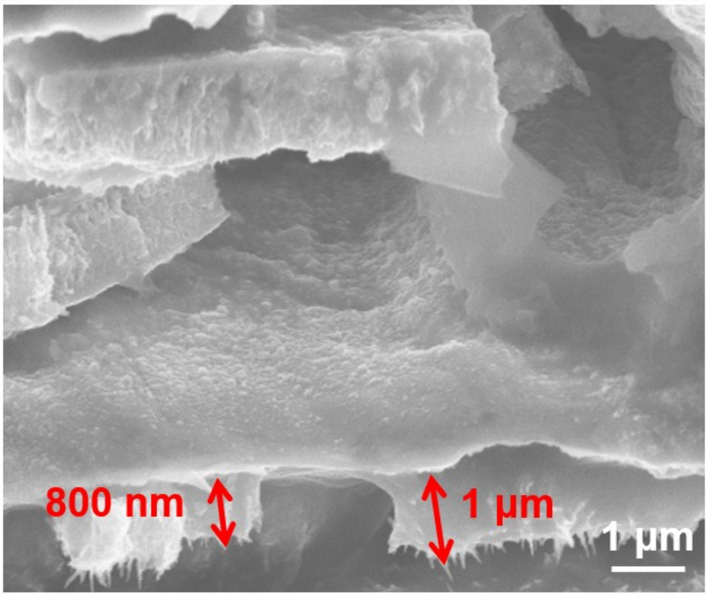

Figure S2. SEM image taken at the cross-section of nickel foam grown with MCO-40 GQDs.

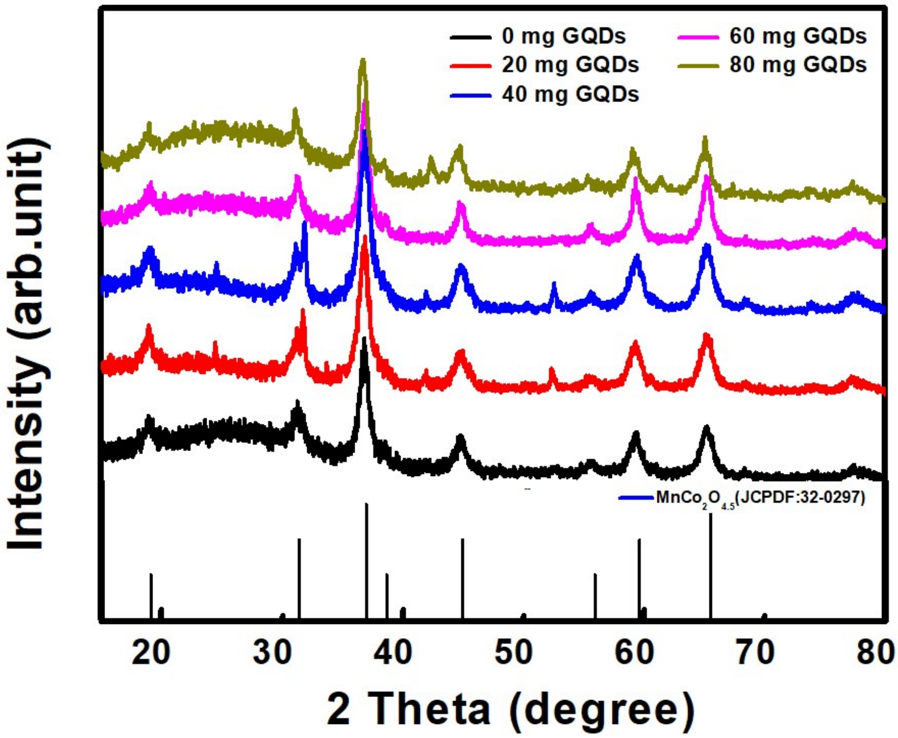

Figure S3. XRD patterns of powders scratched off from $MnCo_2O_{4.5}$ and $MnCo_2O_{4.5}$-X GQDs.

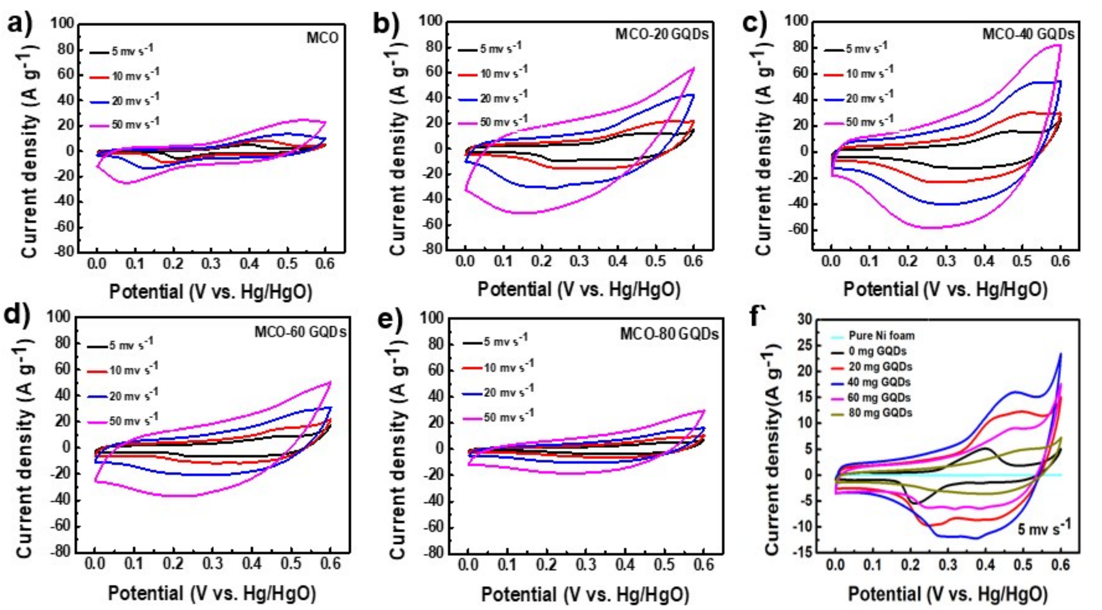

Figure S4. CV curves of a) MCO b) MCO-20 GQDs c) MCO-40 GQDs d) MCO-60 GQDs e) MCO-80 GQDs at different scan rates. f) CV curves of MCO-X GQDs composites and pure Ni foam at scan rate of 5mv s^{-1}

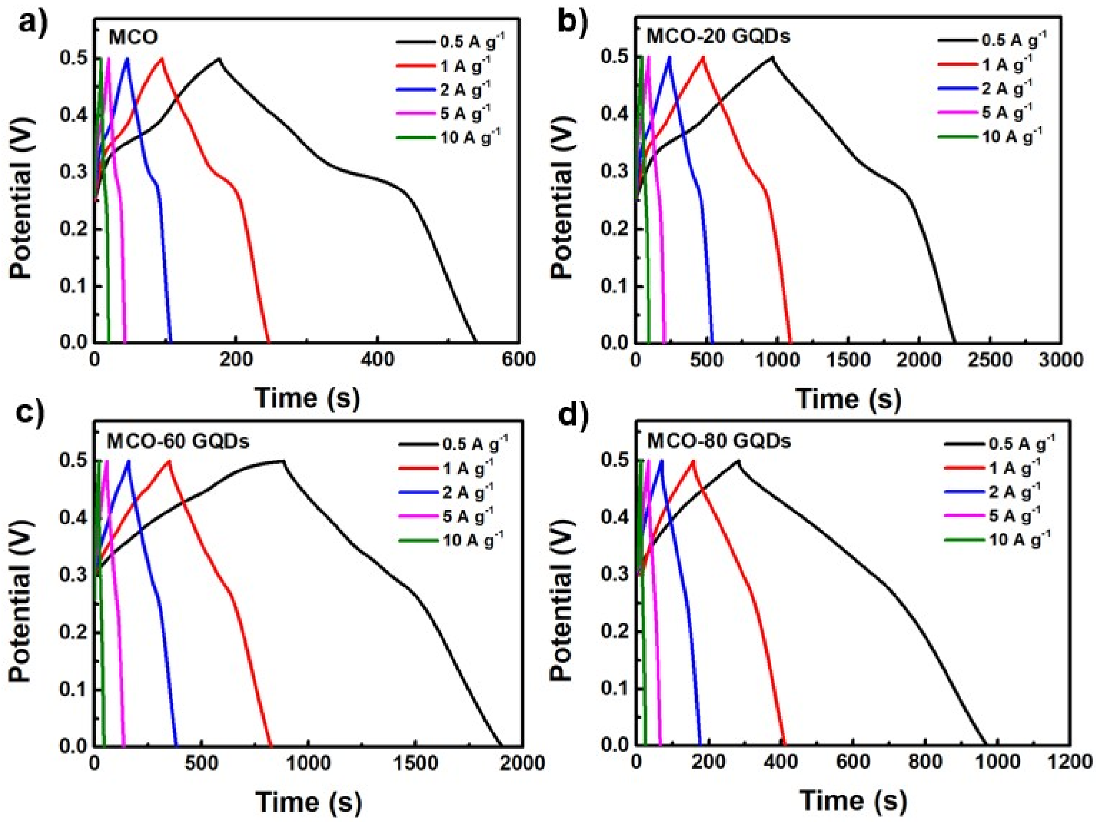

Figure S5. GCD curves of a) MCO b) MCO-20 GQDs c) MCO-60 GQDs d) MCO-80 GQDs at different scan rates.

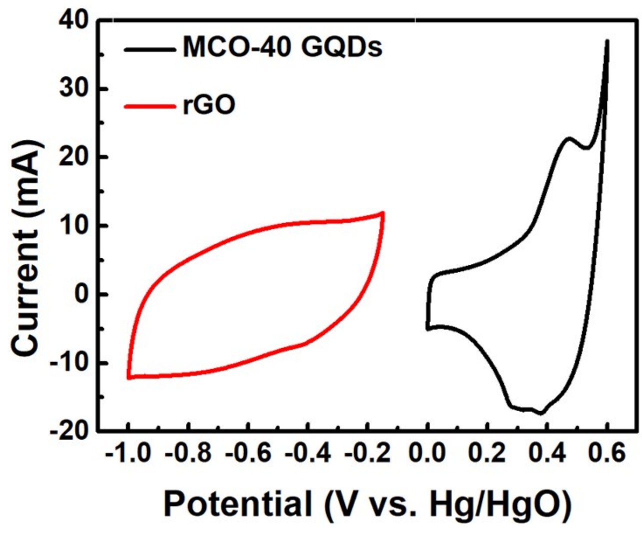

Figure S6. CV curves of rGO and MCO-40 GQDs at scan rate of 5mv s^{-1}

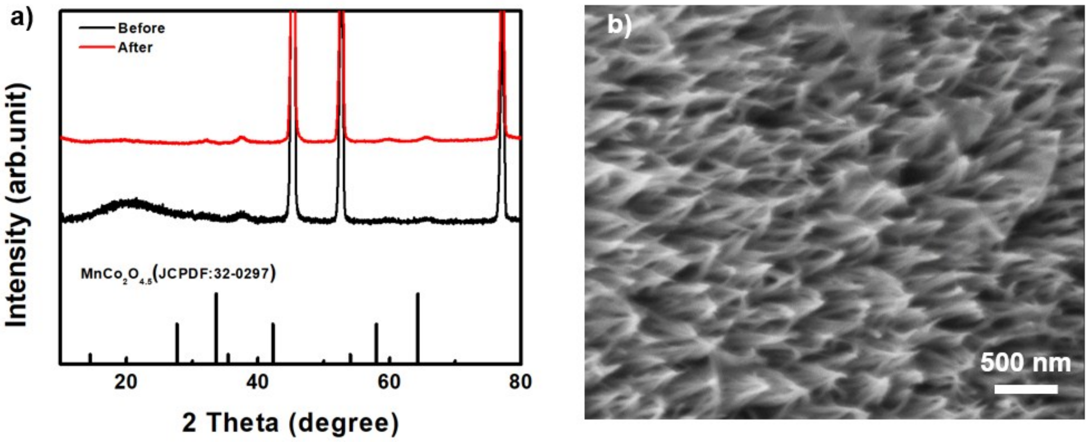

Figure S7. a) XRD spectra of MCO-40 GQDs electrodes before and after cycling, b) SEM image of MCO-40 GQDs electrodes after 5000 cycles of charge and discharge at 1 A g^{-1} in asymmetric MCO-40 GQDs//rGO supercapacitor.

Table S1. Comparison of specific capacitance based on $MnCo_2O_{4.5}$ and $MnCo_2O_4$.

Sample	**Morphology**	**Specific capacitance**	**Current density**	**Reference**
$MnCo_2O_4$	Nanoneedles	1535 F g^{-1}	1 A g^{-1}	14
$MnCo_2O_{4.5}$/carbon aerogel	Nanoneedles	380 F g^{-1}	0.2 A g^{-1}	19
$MnCo_2O_{4.5}$	Nanoneedle arrays	517.9 C g^{-1}	3.6 A g^{-1}	42
$MnCo_2O_{4.5}$@δ-MnO_2	Core/shell	357.5 F g^{-1}	0.5 A g^{-1}	43
$MnCo_2O_4$	Nanosheets	400 F g^{-1}	1 A g^{-1}	44
$MnCo_2O_4$	Nanowires/nanorods	349.8 F g^{-1}	1 A g^{-1}	45
$MnCo_2O_4$	Nanoparticles	405 F g^{-1}	5 mA cm^{-2}	46
$MnCo_2O_4$	Nanowires	1342 F g^{-1}	1 A g^{-1}	47
$MnCo_2O_4$	Flake-like	1487 F g^{-1}	1 A g^{-1}	48
$MnCo_2O_{4.5}$/GQDs	**Nanoneedles**	**1625 F g^{-1}**	**1 A g^{-1}**	**This work**

References

1. Salanne, M.; Rotenberg, B.; Naoi, K.; Kaneko, K.; Taberna, P.-L.; Grey, C. P.; Dunn, B.; Simon, P., Efficient storage mechanisms for building better supercapacitors. *Nature Energy* **2016,** *1* (6), 16070.
2. Raza, W.; Ali, F.; Raza, N.; Luo, Y.; Kwon, E. E.; Yang, J.; Kumar, S.; Mehmood, A.; Kim, K.-H., Recent Advancements in Supercapacitor Technology. *Nano Energy* **2018**.
3. Simon, P.; Gogotsi, Y., Materials for electrochemical capacitors. *Nature materials* **2008,** *7* (11), 845.
4. Liu, L.; Niu, Z.; Chen, J., Unconventional supercapacitors from nanocarbon-based electrode materials to device configurations. *Chemical Society Reviews* **2016,** *45* (15), 4340-4363.
5. Wang, F.; Wu, X.; Yuan, X.; Liu, Z.; Zhang, Y.; Fu, L.; Zhu, Y.; Zhou, Q.; Wu, Y.; Huang, W., Latest advances in supercapacitors: from new electrode materials to novel device designs. *Chemical Society Reviews* **2017,** *46* (22), 6816-6854.
6. Yu, Z.; Tetard, L.; Zhai, L.; Thomas, J., Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions. *Energy & Environmental Science* **2015,** *8* (3), 702-730.
7. Liao, F.; Han, X.; Zhang, Y.; Xu, C.; Chen, H., Solvothermal synthesis of porous MnCo2O4. 5 spindle-like microstructures as high-performance electrode materials for supercapacitors. *Ceramics International* **2018**.
8. Krishnan, S. G.; Reddy, M.; Harilal, M.; Vidyadharan, B.; Misnon, I. I.; Ab Rahim, M. H.; Ismail, J.; Jose, R., Characterization of MgCo2O4 as an electrode for high performance supercapacitors. *Electrochimica Acta* **2015,** *161*, 312-321.
9. Naoi, K.; Simon, P., New materials and new configurations for advanced electrochemical capacitors. *Journal of The Electrochemical Society (JES)* **2008,** *17* (1), 34-37.
10. Dong, Y.; Wang, Y.; Xu, Y.; Chen, C.; Wang, Y.; Jiao, L.; Yuan, H., Facile synthesis of hierarchical nanocage MnCo2O4 for high performance supercapacitor. *Electrochimica Acta* **2017,** *225*, 39-46.
11. Wu, L.; Lang, J.; Zhang, P.; Zhang, X.; Guo, R.; Yan, X., Mesoporous Ni-doped MnCo 2 O 4 hollow nanotubes as an anode material for sodium ion batteries with ultralong life and pseudocapacitive mechanism. *Journal of Materials Chemistry A* **2016,** *4* (47), 18392-18400.
12. Bhagwan, J.; Sivasankaran, V.; Yadav, K.; Sharma, Y., Porous, one-dimensional and high aspect ratio nanofibric network of cobalt manganese oxide as a high performance material for aqueous and solid-state supercapacitor (2 V). *Journal of Power Sources* **2016,** *327*, 29-37.
13. Pettong, T.; Iamprasertkun, P.; Krittayavathananon, A.; Sukha, P.; Sirisinudomkit, P.; Seubsai, A.; Chareonpanich, M.; Kongkachuichay, P.; Limtrakul, J.; Sawangphruk, M., High-performance asymmetric supercapacitors of MnCo2O4 nanofibers and N-doped reduced graphene oxide aerogel. *ACS applied materials & interfaces* **2016,** *8* (49), 34045-34053.
14. Che, H.; Liu, A.; Mu, J.; Wu, C.; Zhang, X., Template-free synthesis of novel flower-like MnCo2O4 hollow microspheres for application in supercapacitors. *Ceramics International* **2016,** *42* (2), 2416-2424.
15. Hui, K. N.; San Hui, K.; Tang, Z.; Jadhav, V.; Xia, Q. X., Hierarchical chestnut-like MnCo2O4 nanoneedles grown on nickel foam as binder-free electrode for high energy density asymmetric supercapacitors. *Journal of Power Sources* **2016,** *330*, 195-203.
16. Li, W.; Xu, K.; Song, G.; Zhou, X.; Zou, R.; Yang, J.; Chen, Z.; Hu, J., Facile synthesis of

porous MnCo 2 O 4.5 hierarchical architectures for high-rate supercapacitors. *CrystEngComm* **2014,** *16* (12), 2335-2339.

17. Fu, Y.; He, H.; Li, X.; Wu, L.; Yan, R.; Zhang, J.; Xu, X.; Wang, F., Enhance supercapacitive performance of Ni foam electrode and MnCo 2 O 4.5/Ni foam electrode. *Journal of Materials Science: Materials in Electronics* **2017,** *28* (2), 1562-1571.

18. Borenstein, A.; Hanna, O.; Attias, R.; Luski, S.; Brousse, T.; Aurbach, D., Carbon-based composite materials for supercapacitor electrodes: a review. *Journal of Materials Chemistry A* **2017,** *5* (25), 12653-12672.

19. Tian, J.; Liu, Q.; Asiri, A. M.; Sun, X., Self-supported nanoporous cobalt phosphide nanowire arrays: an efficient 3D hydrogen-evolving cathode over the wide range of pH 0–14. *Journal of the American Chemical Society* **2014,** *136* (21), 7587-7590.

20. Hao, P.; Zhao, Z.; Li, L.; Tuan, C.-C.; Li, H.; Sang, Y.; Jiang, H.; Wong, C.; Liu, H., The hybrid nanostructure of MnCo 2 O 4.5 nanoneedle/carbon aerogel for symmetric supercapacitors with high energy density. *Nanoscale* **2015,** *7* (34), 14401-14412.

21. Li, Y.; Peng, X.; Xiang, J.; Yang, J., Synthesis of MnCo2O4. 5/graphene Composite as Electrode Material for Supercapacitors. *INTERNATIONAL JOURNAL OF ELECTROCHEMICAL SCIENCE* **2017,** *12* (11), 10763-10772.

22. Ponomarenko, L.; Schedin, F.; Katsnelson, M.; Yang, R.; Hill, E.; Novoselov, K.; Geim, A., Chaotic Dirac billiard in graphene quantum dots. *Science* **2008,** *320* (5874), 356-358.

23. Zhang, Z.; Zhang, J.; Chen, N.; Qu, L., Graphene quantum dots: an emerging material for energy-related applications and beyond. *Energy & Environmental Science* **2012,** *5* (10), 8869-8890.

24. Ganganboina, A. B.; Dutta Chowdhury, A.; Doong, R.-a., New avenue for appendage of graphene quantum dots on halloysite nanotubes as anode materials for high performance supercapacitors. *ACS Sustainable Chemistry & Engineering* **2017,** *5* (6), 4930-4940.

25. Chen, L.; Guo, C. X.; Zhang, Q.; Lei, Y.; Xie, J.; Ee, S.; Guai, G.; Song, Q.; Li, C. M., Graphene quantum-dot-doped polypyrrole counter electrode for high-performance dye-sensitized solar cells. *ACS applied materials & interfaces* **2013,** *5* (6), 2047-2052.

26. Jia, H.; Cai, Y.; Lin, J.; Liang, H.; Qi, J.; Cao, J.; Feng, J.; Fei, W., Heterostructural Graphene Quantum Dot/MnO2 Nanosheets toward High-Potential Window Electrodes for High-Performance Supercapacitors. *Advanced Science* **2018**.

27. Mondal, S.; Rana, U.; Malik, S., Graphene quantum dot-doped polyaniline nanofiber as high performance supercapacitor electrode materials. *Chemical Communications* **2015,** *51* (62), 12365-12368.

28. Qing, Y.; Jiang, Y.; Lin, H.; Wang, L.; Liu, A.; Cao, Y.; Sheng, R.; Guo, Y.; Fan, C.; Zhang, S., Boosting the Supercapacitor Performance of Activated Carbon by Constructing Overall Conductive Networks Using Graphene Quantum Dots. *Journal of Materials Chemistry A* **2019**.

29. Dong, Y.; Shao, J.; Chen, C.; Li, H.; Wang, R.; Chi, Y.; Lin, X.; Chen, G., Blue luminescent graphene quantum dots and graphene oxide prepared by tuning the carbonization degree of citric acid. *Carbon* **2012,** *50* (12), 4738-4743.

30. Meher, S. K.; Rao, G. R., Ultralayered Co3O4 for high-performance supercapacitor applications. *The Journal of Physical Chemistry C* **2011,** *115* (31), 15646-15654.

31. Lee, H.-M.; Chandu, V. M. G.; Rana, P. J. S.; Vinodh, R.; Kim, S.; Rapur, P.; Kim, H.-J., Hierarchical nanostructured MnCo2O4-NiCo2O4 composite as an innovative electrode for supercapacitor applications. *New Journal of Chemistry* **2018**.

32. Liu, S.; San Hui, K.; Hui, K. N.; Yun, J. M.; Kim, K. H., Vertically stacked bilayer CuCo 2 O

4/MnCo 2 O 4 heterostructures on functionalized graphite paper for high-performance electrochemical capacitors. *Journal of Materials Chemistry A* **2016,** *4* (21), 8061-8071.
33. Pan, D.; Zhang, J.; Li, Z.; Wu, M., Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots. *Advanced materials* **2010,** *22* (6), 734-738.
34. Li, L.; Wu, G.; Yang, G.; Peng, J.; Zhao, J.; Zhu, J.-J., Focusing on luminescent graphene quantum dots: current status and future perspectives. *Nanoscale* **2013,** *5* (10), 4015-4039.
35. Gu, J.; Zhang, X.; Pang, A.; Yang, J., Facile synthesis and photoluminescence characteristics of blue-emitting nitrogen-doped graphene quantum dots. *Nanotechnology* **2016,** *27* (16), 165704.
36. Lin, L.; Rong, M.; Luo, F.; Chen, D.; Wang, Y.; Chen, X., Luminescent graphene quantum dots as new fluorescent materials for environmental and biological applications. *TrAC Trends in Analytical Chemistry* **2014,** *54*, 83-102.
37. Wang, S.; Chen, Z.-G.; Cole, I.; Li, Q., Structural evolution of graphene quantum dots during thermal decomposition of citric acid and the corresponding photoluminescence. *Carbon* **2015,** *82*, 304-313.
38. Ye, R.; Xiang, C.; Lin, J.; Peng, Z.; Huang, K.; Yan, Z.; Cook, N. P.; Samuel, E. L.; Hwang, C.-C.; Ruan, G., Coal as an abundant source of graphene quantum dots. *Nature communications* **2013,** *4*, 2943.
39. Zheng, P.; Wu, N., Fluorescence and sensing applications of graphene oxide and graphene quantum dots: a review. *Chemistry–An Asian Journal* **2017,** *12* (18), 2343-2353.
40. Thorat, G. M.; Jadhav, H. S.; Seo, J. G., Bi-functionality of mesostructured MnCo2O4 microspheres for supercapacitor and methanol electro-oxidation. *Ceramics International* **2017,** *43* (2), 2670-2679.
41. Wei, G.; Zhao, X.; Du, K.; Huang, Y.; An, C.; Qiu, S.; Liu, M.; Yao, S.; Wu, Y., Flexible asymmetric supercapacitors made of 3D porous hierarchical CuCo2O4@ CQDs and Fe2O3@ CQDs with enhanced performance. *Electrochimica Acta* **2018,** *283*, 248-259.
42. Wei, J. S.; Ding, H.; Zhang, P.; Song, Y. F.; Chen, J.; Wang, Y. G.; Xiong, H. M., Carbon dots/NiCo2O4 nanocomposites with various morphologies for high performance supercapacitors. *Small* **2016,** *12* (43), 5927-5934.
43. Li, Y.; Hu, Y.; Zhao, Y.; Shi, G.; Deng, L.; Hou, Y.; Qu, L., An electrochemical avenue to green-luminescent graphene quantum dots as potential electron-acceptors for photovoltaics. *Advanced materials* **2011,** *23* (6), 776-780.
44. Ni, L.; Tang, W.; Liu, X.; Zhang, N.; Wang, J.; Liang, S.; Ma, R.; Qiu, G., Hierarchical CoO/MnCo 2 O 4.5 nanorod arrays on flexible carbon cloth as high-performance anode materials for lithium-ion batteries. *Dalton Transactions* **2018,** *47* (11), 3775-3784.
45. Zhu, J.; Wang, S.; Wang, J.; Zhang, D.; Li, H., Highly active and durable Bi2O3/TiO2 visible photocatalyst in flower-like spheres with surface-enriched Bi2O3 quantum dots. *Applied Catalysis B: Environmental* **2011,** *102* (1-2), 120-125.
46. Dey, T.; Mukherjee, S.; Ghorai, A.; Das, S.; Ray, S. K., Surface state selective tunable emission of graphene quantum dots exhibiting novel thermal quenching characteristics. *Carbon* **2018,** *140*, 394-403.
47. Zhu, Y.; Ji, X.; Pan, C.; Sun, Q.; Song, W.; Fang, L.; Chen, Q.; Banks, C. E., A carbon quantum dot decorated RuO 2 network: outstanding supercapacitances under ultrafast charge and discharge. *Energy & Environmental Science* **2013,** *6* (12), 3665-3675.
48. Zhu, Y.; Wu, Z.; Jing, M.; Hou, H.; Yang, Y.; Zhang, Y.; Yang, X.; Song, W.; Jia, X.; Ji, X.,

Porous $NiCo_2O_4$ spheres tuned through carbon quantum dots utilised as advanced materials for an asymmetric supercapacitor. *Journal of Materials Chemistry A* **2015,** *3* (2), 866-877.
49. Kuang, L.; Ji, F.; Pan, X.; Wang, D.; Chen, X.; Jiang, D.; Zhang, Y.; Ding, B., Mesoporous $MnCo_2O_{4.5}$ nanoneedle arrays electrode for high-performance asymmetric supercapacitor application. *Chemical Engineering Journal* **2017,** *315*, 491-499.
50. Li, F.; Li, G.; Chen, H.; Jia, J. Q.; Dong, F.; Hu, Y. B.; Shang, Z. G.; Zhang, Y. X., Morphology and crystallinity-controlled synthesis of manganese cobalt oxide/manganese dioxides hierarchical nanostructures for high-performance supercapacitors. *Journal of Power Sources* **2015,** *296*, 86-91.
51. Xu, Y.; Wang, X.; An, C.; Wang, Y.; Jiao, L.; Yuan, H., Facile synthesis route of porous $MnCo_2O_4$ and $CoMn_2O_4$ nanowires and their excellent electrochemical properties in supercapacitors. *Journal of Materials Chemistry A* **2014,** *2* (39), 16480-16488.
52. Mondal, A. K.; Su, D.; Chen, S.; Ung, A.; Kim, H. S.; Wang, G., Mesoporous $MnCo_2O_4$ with a Flake-Like Structure as Advanced Electrode Materials for Lithium-Ion Batteries and Supercapacitors. *Chemistry–A European Journal* **2015,** *21* (4), 1526-1532.
53. Nguyen, T.; Boudard, M.; Rapenne, L.; Chaix-Pluchery, O.; Carmezim, M. J.; Montemor, M. F., Structural evolution, magnetic properties and electrochemical response of $MnCo_2O_4$ nanosheet films. *RSC Advances* **2015,** *5* (35), 27844-27852.
54. Kong, L.-B.; Lu, C.; Liu, M.-C.; Luo, Y.-C.; Kang, L.; Li, X.; Walsh, F. C., The specific capacitance of sol–gel synthesised spinel $MnCo_2O_4$ in an alkaline electrolyte. *Electrochimica Acta* **2014,** *115*, 22-27.
55. Li, L.; Zhang, Y.; Liu, X.; Shi, S.; Zhao, X.; Zhang, H.; Ge, X.; Cai, G.; Gu, C.; Wang, X., One-dimension $MnCo_2O_4$ nanowire arrays for electrochemical energy storage. *Electrochimica Acta* **2014,** *116*, 467-474.
56. Sahoo, S.; Naik, K. K.; Rout, C. S., Electrodeposition of spinel $MnCo_2O_4$ nanosheets for supercapacitor applications. *Nanotechnology* **2015,** *26* (45), 455401.
57. Wang, Y.-M.; Zhang, X.; Guo, C.-Y.; Zhao, Y.-Q.; Xu, C.-L.; Li, H.-L., Controllable synthesis of 3D $Ni_{\chi}Co_{1-\chi}$ oxides with different morphologies for high-capacity supercapacitors. *Journal of Materials Chemistry A* **2013,** *1* (42), 13290-13300.
58. Zhu, Y.; Wu, Z.; Jing, M.; Yang, X.; Song, W.; Ji, X., Mesoporous $NiCo_2S_4$ nanoparticles as high-performance electrode materials for supercapacitors. *Journal of Power Sources* **2015,** *273*, 584-590.
59. Xu, K.; Li, W.; Liu, Q.; Li, B.; Liu, X.; An, L.; Chen, Z.; Zou, R.; Hu, J., Hierarchical mesoporous $NiCo_2O_4$@MnO_2 core–shell nanowire arrays on nickel foam for aqueous asymmetric supercapacitors. *Journal of Materials Chemistry A* **2014,** *2* (13), 4795-4802.