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

Supporting Information

Highly Efficient 3D Graphene-CNTs-MnO_2-PANI Nanocomposite Synthesis as Binder Free Electrode Material for Supercapacitors

Muhammad Asif[a,b,*], Yi Tan[a], Lujun Pan[b1*], Muhammad Rashad[c], Jiayan Li[a], Xin Fu[b], Ruixue Cui[b]

a School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, PR China

b School of Physics and Optoelectronic Technology, Dalian University of Technology, Dalian 116024, PR China

c Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116024, PR China.

[1]* Corresponding Authors: Fax: +86 411 84709304

Email Address: asifnust86@gmail.com (M. Asif)

lpan@dlut.edu.cn (L. Pan),

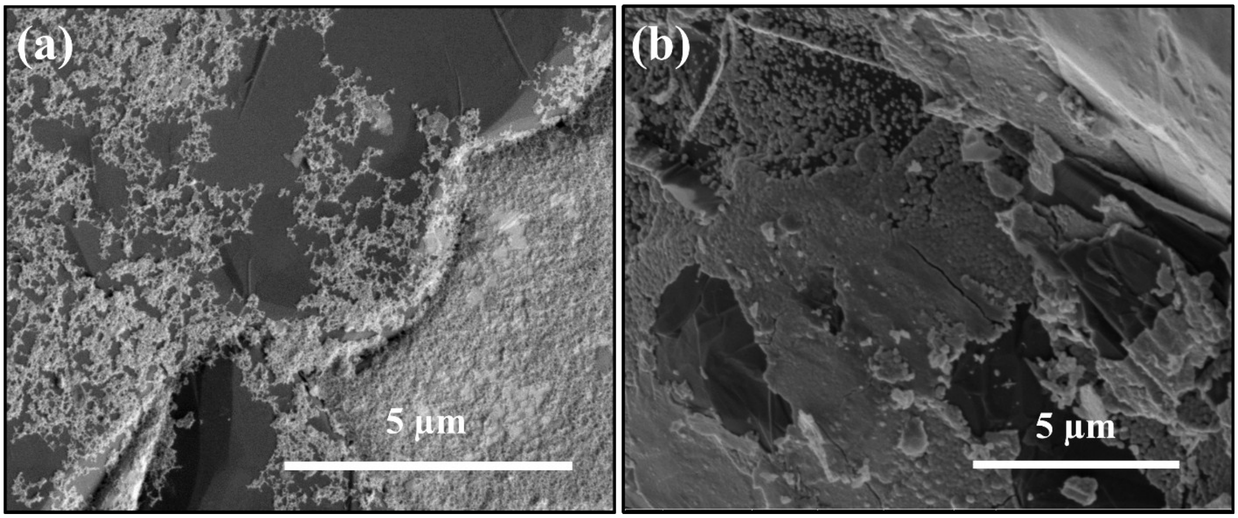

Figure S.1. SEM micrographs for G@MnO_2 (a), and GCM@PANI nanocomposite (b).

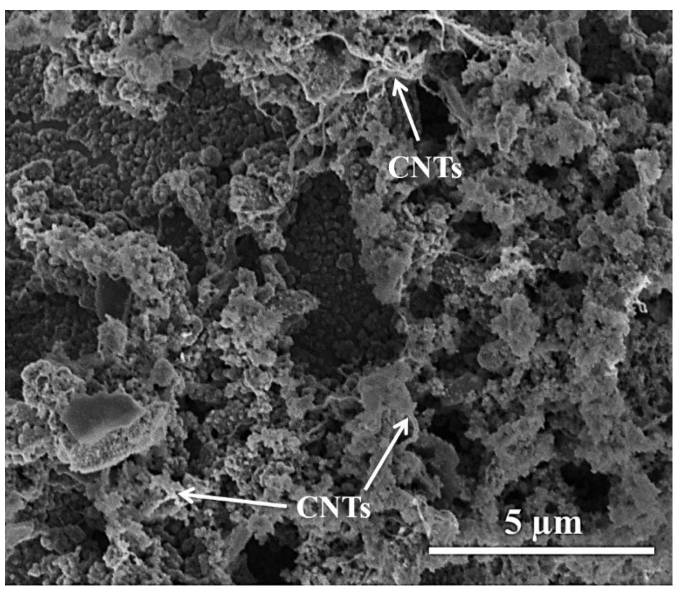

Figure S.2. FESEM micrographs for GCM@PANI nanocomposite taken from area where agglomeration of nanostructures exist. This sample is one without optimized conditions.

The FESEM image in Figure S.2 illustrates nucleation of MnO_2 nanostructures around MWCNTs. This sample was taken out of solution without completing synthesis procedure.

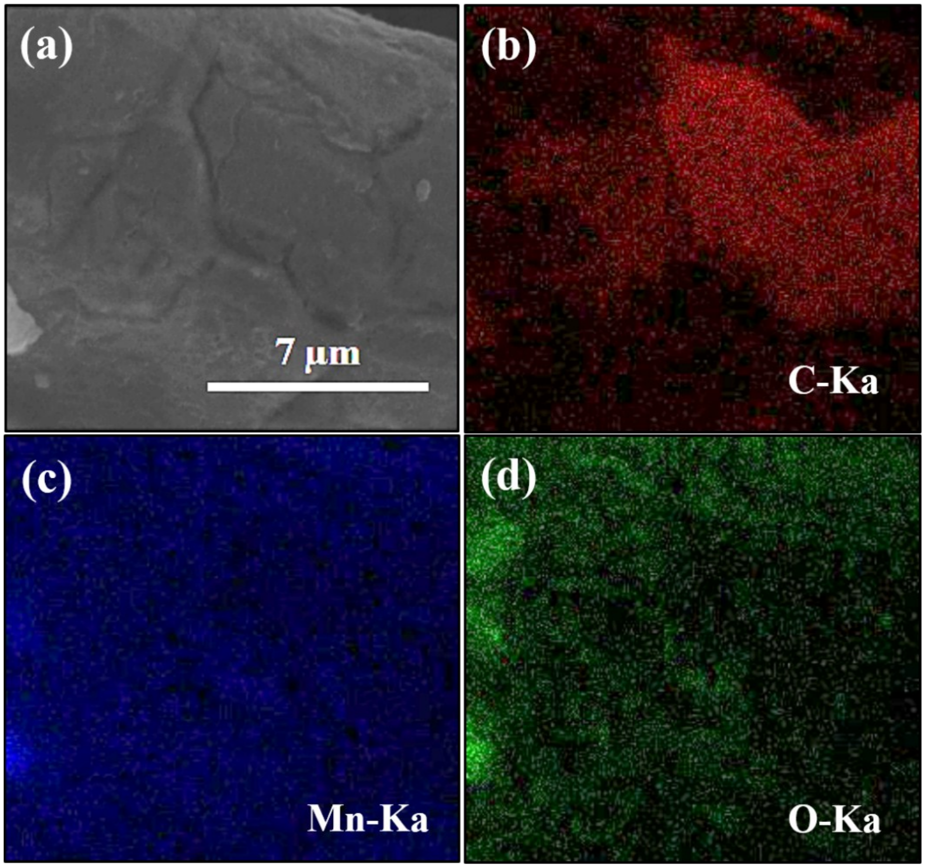

Figure S.3. (a) FESEM micrograph of GCM@PANI, (b-d) EDS mapping for elements C, Mn, and O, respectively.

Table S.1. Elemental composition (at.%) of C, N, O, and Mn estimated from XPS quantitative analysis.

Composite	C	N	O	Mn	C/N ratio
GM@PANI[1]	71.03	1.22	22.87	4.88	58.22
GCM@PANI	68.83	1.42	23.7	6.05	48.47

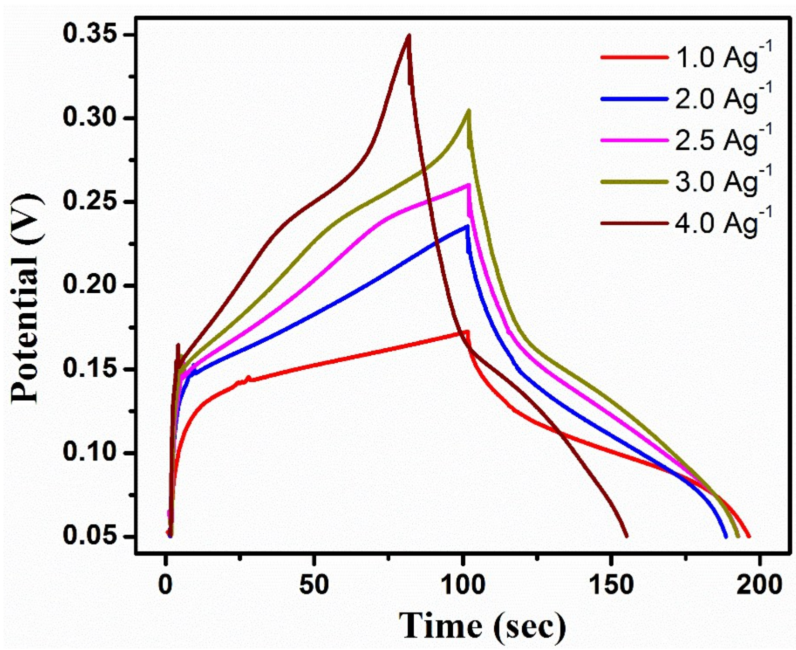

Figure S.4. Galvanostatic CD curves for non-activated GCM@PANI nanocomposite at different current densities.

The galvanostatic SC for the non-activated GCM@PANI nanocomposite was calculated to be 300, 785, 867942, 1086, 1071, 1040, 1002, 985, and 928 Fg^{-1} at 0.5, 1.5, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 10.0 Ag^{-1} current densities, respectively. However, the galvanostatic SC for the activated GCM@PANI nanocomposite was measured to be 795, 1019, 1332, 2015, 2402, 2757, 2949, 3037, 2989, 2958, 2891, 2730, 2569, 2060, 1450, 1061, and 784 Fg^{-1} at current densities 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 12.0, 15.0, 20.0, 30.0, 50.0, 75.0, and 100.0 Ag^{-1}.

The galvanostatic SC for the activated GC@MnO_2 nanocomposite was measured to be 832 Fg^{-1} at 2.5 Ag^{-1} current density, which will be reported somewhere else.

Table S.2. Electrochemical Performances for Graphene, CNTs, MnO_2, and PANI nanomaterials in different nanocomposites.

Electrode Materials	Electrolyte	SC_{max} (Fg^{-1})	Rate Capability (Fg^{-1})	Stability (cycles)	Ref.
3D G	1 M Organic	198 (Ag^{-1})	58 (100 Ag^{-1})	88% (1000)	2
G/Act. C	6 M KOH	210 (1 mVs^{-1})	-	94.7% (5000)	3
MnO_2/CNT	1 M Na_2SO_4	994 (1 mV/S)	544 (500 mVs^{-1})	94.6% (500)	4
MnO_2/CNT	1 M NaCl	309 (2 mV/S)	221 (500 mVs^{-1})	96% (10,000)	5
MnO_2/CNT	1 M K_2SO_4	1.0 Fcm^{-1} (0.2 Ag^{-1})	77% (20 Ag^{-1})	100 % (3000)	6
MnO_2/CNT	6 M Na_2SO_4	185 (5 mVs^{-1})	117 (100 mVs^{-1})	94% (2000)	7
MnO_2/CNT	1 M Na_2SO_4	325.5 (0.3 Ag^{-1})	70.7%	90.5% (5000)	8
MnO_2 NP/G	1 M Na_2SO_4	324 (10 mV/S)	276 (150 mVs^{-1})	96.8% (1000)	9
MnO_2/N-rGO	1 M Na_2SO_4	275.2 (2 $mAcm^{-2}$)	-	98.3% (1000)	10
MnO_2/G	6 M KOH	479 (1 Ag^{-1})	313 (10 Ag^{-1})	83.5% (1000)	11
MnO_2 HS/G	1 M KOH	578 (0.5 Ag^{-1})	110 (1.75 Ag^{-1})	--	12
PANI NW/G	1 M H_2SO_4	630 (0.5 Ag^{-1})	80% (10 Ag^{-1})	90.5% (5000)	13
PANI Arrays/G		844 (0.5 Ag^{-1})	625 (2 Ag^{-1})	76% (1000)	14
PANI/ rGO	1 M H_2SO_4	740 (0.5 Ag^{-1})	58% (10 Ag^{-1})	87% (1000)	15
PANI/G	1 M H_2SO_4	749 (0.5 Ag^{-1})	73% (5 Ag^{-1})	88% (1000)	16
PANI/MWCNTs	1 M H_2SO_4	609 (0.1 $mAcm^{-2}$)	543 (1.0 $mAcm^{-2}$)	77% (1500)	17
PANI NW/3D C	1 M H_2SO_4	1192 (0.5 Ag^{-1})	66.4% (100 Ag^{-1})	83% (1000)	18
MnO_2/PANI	1 M Na_2SO_4	687 (5 mVs^{-1})	--	95% (2000)	19
MnO_2/PANI	1 M Na_2SO_4	873 (0.25 Ag^{-1})	1184 (1.25 Ag^{-1})	95% (5000)	20
MnO_2/PANI	1 M H_2SO_4	626 (2 Ag^{-1})	480 (20 Ag^{-1})	70% (1000)	21
PANI/Co_3O_4	6 M KOH	1184 (1.25 Ag^{-1})	500 (50 Ag^{-1})	85% (1000)	22

PANI NW/TiO_2 NT	0.05 M H_2SO_4	897 (0.21 Ag^{-1})	--	86% (1500)	23
G/NiOOH	2 M KOH	1162 (1 Ag^{-1})	981 (20 Ag^{-1})	85.3% (8000)	24
GO/$CoNi(OH)_2$	1 M KOH	1359 (1 Ag^{-1})	1075 (100 Ag^{-1})	72% (7000)	25
MnO_2/Co_3O_4	1 M LiOH	560 (0.2 Ag^{-1})	54% (10 Ag^{-1})	95% (5000)	26
Co_3O_4@$CoMoO_4$	PVA/KOH gel	1902 (1 Ag^{-1})	1200 (10 Ag^{-1})	99% (5000)	27
rG/PANI/$CoFe_2O_4$	1 M KOH	768 (0.1 Ag^{-1})	330 (3 Ag^{-1})	96% (5000)	28
MnO_2/PANI/CNT	0.5 M Na_2SO_4	384 (2.5 $mAcm^{-2}$)	267 (13.5 $mAcm^{-2}$)	80% (1000)	29
MnO_2/CNT/G	1 M Na_2SO_4	193 (0.2 Ag^{-1})	105 (5 Ag^{-1})	70% (1300)	30
MnO_2/CNT/G	30% KOH	325 (5 mVs^{-1})	285 (200 mVs^{-1})	90% (5000)	31
MnO_2/CNT/G	1 M Na_2SO_4	126 (0.25 Ag^{-1})	112 (4 Ag^{-1})	-	32
MnO_2/CNT/G	1 M Na_2SO_4	319 (0.5 Ag^{-1})	222 (60 Ag^{-1})	85.4% (3000)	33
MnO_2/CNT/G	1 M Na_2SO_4	245 (0.5 Ag^{-1})	73 (20 Ag^{-1})	91.4% (2000)	34
MnO_2/CNT/G	1 M Na_2SO_4	255 (0.5 Ag^{-1})	150 (20 Ag^{-1})	83% (1000)	35
MnO_2/PPy/G	1 M Na_2SO_4	469.5 (0.3 Ag^{-1})	312 (1.5 Ag^{-1})	77% (1000)	36
MnO_2/PANI/sG	1 M Na_2SO_4	276 (1 g^{-1})	73% (20 Ag^{-1})	88.3% (3000)	37
MnO_2/PANI/G	1 M Na_2SO_4	512 (0.25 Ag^{-1})	62% (4 Ag^{-1})	97% (5000)	38
MnO_2/PANI/G	1 M KOH	455 (0.2 Ag^{-1})	75.8% (5 Ag^{-1})	76.4% (5000)	39
MnO_2/PANI/G	6 M NaOH	276 (0.08 Ag^{-1})	94.7 (1.25 Ag^{-1})	96% (3000)	40
MnO_2/PANI/G	0.5 M Na_2SO_4	755 (0.5 Ag^{-1})	568 (10 Ag^{-1})	87% (1000)	41
MnO_2/PANI/G	1 M H_2SO_4	800 (0.4 Ag^{-1})	505 (10 Ag^{-1})	71% (800)	42
MnO_2/PANI/G	1 M Na_2SO_4	875 (0.2 Ag^{-1})	695 (4 Ag^{-1})	93% (1000)	43
MnO_2/PANI/3DG	**6 M KOH**	**1369 (3 Ag^{-1})**	**70% (15 Ag^{-1})**	**83% (5000)**	**Previous work [1]**
MnO2/PANI/CNTs/3DG	**6 M KOH**	**3037 (8 Ag^{-1})**	**84.6% (20 Ag^{-1})**	**83% (12000)**	**Current Work**

rG: reduced graphene; CNT: carbon nanotubes; PANI: poly aniline; 3D: three dimensional;

NW: nano wires; NA: nano arrays; Act. C: activated carbon;

References:

1. M. Asif, Y. Tan, L. Pan, J. Li, M. Rashad, X. Fu, R. Cui and M. Usman, *RSC Adv.*, 2016, **6**, 46100-46107.
2. X.-F. Jiang, X.-B. Wang, P. Dai, X. Li, Q. Weng, X. Wang, D.-M. Tang, J. Tang, Y. Bando and D. Golberg, *Nano Energy*, 2015, **16**, 81-90.
3. C. Zheng, X. Zhou, H. Cao, G. Wang and Z. Liu, *J. Power Sources*, 2014, **258**, 290-296.
4. J. Yan, Z. Fan, T. Wei, J. Cheng, B. Shao, K. Wang, L. Song and M. Zhang, *J. Power Sources*, 2009, **194**, 1202-1207.
5. Y.-P. Lin, C.-B. Tsai, W.-H. Ho and N.-L. Wu, *Mater. Chem. Phys.*, 2011, **130**, 367-372.
6. K. Wang, S. Gao, Z. Du, A. Yuan, W. Lu and L. Chen, *J. Power Sources*, 2016, **305**, 30-36.
7. R. S. Rahul, A. Heejoon, K. Jung Ho and Y. Yusuke, *Nanotechnology*, 2015, **26**, 204004.
8. M. Huang, R. Mi, H. Liu, F. Li, X. L. Zhao, W. Zhang, S. X. He and Y. X. Zhang, *J. Power Sources*, 2014, **269**, 760-767.
9. Y. Qian, S. Lu and F. Gao, *J. Mater. Sci.*, 2011, **46**, 3517-3522.
10. J. Mei and L. Zhang, *Electrochim. Acta*, 2015, **173**, 338-344.
11. Y. Sun, W. Zhang, D. Li, L. Gao, C. Hou, Y. Zhang and Y. Liu, *J. Alloy. Compd.*, 2015, **649**, 579-584.
12. H. Chen, S. Zhou, M. Chen and L. Wu, *J. Mater. Chem.*, 2012, **22**, 25207-25216.
13. S. Wang, L. Ma, M. Gan, S. Fu, W. Dai, T. Zhou, X. Sun, H. Wang and H. Wang, *Synth. Met.*, 2015, **210**, 367-375.
14. H. Mi, J. Zhou, Q. Cui, Z. Zhao, C. Yu, X. Wang and J. Qiu, *Carbon*, 2014, **80**, 799-807.
15. S. Wang, L. Ma, M. Gan, S. Fu, W. Dai, T. Zhou, X. Sun, H. Wang and H. Wang, *J. Power Sources*, 2015, **299**, 347-355.
16. Q. Wang, J. Yan, Z. Fan, T. Wei, M. Zhang and X. Jing, *J. Power Sources*, 2014, **247**, 197-203.
17. P.-Y. Chen, N.-M. Dorval Courchesne, M. N. Hyder, J. Qi, A. M. Belcher and P. T. Hammond, *RSC Adv.*, 2015, **5**, 37970-37977.
18. H. Hu, S. Liu, M. Hanif, S. Chen and H. Hou, *J. Power Sources*, 2014, **268**, 451-458.
19. A. Nirmalesh Naveen and S. Selladurai, *Mat. Sci. Semicon. Proc*, 2015, **40**, 468-478.
20. A. Sumboja, C. Y. Foo, J. Yan, C. Yan, R. K. Gupta and P. S. Lee, *J. Mater. Chem.*, 2012, **22**, 23921-23928.
21. Jaidev, R. I. Jafri, A. K. Mishra and S. Ramaprabhu, *J. Mater. Chem.*, 2011, **21**, 17601-17605.
22. Z. Hai, L. Gao, Q. Zhang, H. Xu, D. Cui, Z. Zhang, D. Tsoukalas, J. Tang, S. Yan and C. Xue, *Appl. Surf. Sci.*, 2016, **361**, 57-62.
23. Z. Shao, H. Li, M. Li, C. Li, C. Qu and B. Yang, *Energy*, 2015, **87**, 578-585.
24. R. Wang, C. Xu and J.-M. Lee, *Nano Energy*, 2016, **19**, 210-221.
25. F. Grote, Z.-Y. Yu, J.-L. Wang, S.-H. Yu and Y. Lei, *Small*, 2015, **11**, 4666-4672.
26. M. Huang, Y. Zhang, F. Li, L. Zhang, Z. Wen and Q. Liu, *J. Power Sources*, 2014, **252**, 98-106.
27. J. Wang, X. Zhang, Q. Wei, H. Lv, Y. Tian, Z. Tong, X. Liu, J. Hao, H. Qu, J. Zhao, Y. Li and L. Mai, *Nano Energy*, 2016, **19**, 222-233.
28. P. Xiong, H. Huang and X. Wang, *J. Power Sources*, 2014, **245**, 937-946.
29. C. Yuan, L. Su, B. Gao and X. Zhang, *Electrochim. Acta*, 2008, **53**, 7039-7047.

30. Z. Lei, F. Shi and L. Lu, *ACS Appl. Mater. Interfaces*, 2012, **4**, 1058-1064.
31. R. B. Rakhi, W. Chen, D. Cha and H. N. Alshareef, *Advanced Energy Materials*, 2012, **2**, 381-389.
32. L. Deng, Z. Hao, J. Wang, G. Zhu, L. Kang, Z.-H. Liu, Z. Yang and Z. Wang, *Electrochim. Acta*, 2013, **89**, 191-198.
33. H. Jiang, Y. Dai, Y. Hu, W. Chen and C. Li, *ACS Sustainable Chemistry & Engineering*, 2014, **2**, 70-74.
34. J. Chen, Y. Huang, X. Zhang, X. Chen and C. Li, *Ceram. Int.*, 2015, **41**, 12680-12685.
35. Y. Xiong, M. Zhou, H. Chen, L. Feng, Z. Wang, X. Yan and S. Guan, *Appl. Surf. Sci.*, 2015, **357, Part A**, 1024-1030.
36. J. An, J. Liu, Y. Ma, R. Li, M. Li, M. Yu and S. Li, *Eur. Phys. J. Appl. Phys.*, 2012, **58**, 30403.
37. G. Wang, Q. Tang, H. Bao, X. Li and G. Wang, *J. Power Sources*, 2013, **241**, 231-238.
38. G. Han, Y. Liu, L. Zhang, E. Kan, S. Zhang, J. Tang and W. Tang, *Sci. Rep.*, 2014, **4**, 4824.
39. P. Xiong, C. Hu, Y. Fan, W. Zhang, J. Zhu and X. Wang, *J. Power Sources*, 2014, **266**, 384-392.
40. Z. Bai, H. Li, M. Li, C. Li, X. Wang, C. Qu and B. Yang, *Int. J. Hydrogen. Energ*, 2015, **40**, 16306-16315.
41. L. Yu, M. Gan, L. Ma, H. Huang, H. Hu, Y. Li, Y. Tu, C. Ge, F. Yang and J. Yan, *Synth. Met.*, 2014, **198**, 167-174.
42. K. Li, D. Guo, J. Chen, Y. Kong and H. Xue, *Synth. Met.*, 2015, **209**, 555-560.
43. C. Pan, H. Gu and L. Dong, *J. Power Sources*, 2016, **303**, 175-181.