

Efficient reduction of graphene oxide using Tin-powder and its electrochemical performances for energy storage electrode material

Nam Hoon Kim,^a Partha Khanra,^a Tapas Kuila,^b Joong Hee Lee,^{c,d*}

^aWCU Program, Department of BIN Fusion Technology, Chonbuk National University, Jeonju, Jeonbuk, 561-756, Republic of Korea

^bSurface Engineering & Tribology Division, CSIR-Central Mechanical Engineering Research Institute, Council of Scientific & Industrial Research (CSIR), Mahatma Gandhi Avenue, Durgapur -713209, India

^cBIN Fusion Research Center, Department of Polymer & Nano Engineering, Chonbuk National University, Jeonju, Jeonbuk, 561-756, Republic of Korea

^dDepartment of Hydrogen and Fuel Cell Engineering, Chonbuk National University, Jeonju, Jeonbuk, 561-756, Republic of Korea.

*Correspondence to: Prof. Joong Hee Lee(jhl@jbnu.ac.kr)

Table S1 Comparison of properties of reduced GOs produced by various reducing agents

Reducing agent	Temperature (°C)	Reduction Time	C:O ratio by XPS (atomic ratio)	Electrical conductivity (S m ⁻¹)	Specific capacitance (F g ⁻¹)	Reference No
Al(powder)/ HCl	RT	30 min	18.6	2,100	-----	1
Al(foil)/HCl	RT	6 h	21.11	12,530	-----	2
Al(foil)/NaOH	RT	30 min	5.35	1,120	-----	2
Fe(powder)/ HCl	RT	6 h	7.9	2,300	-----	3
Zn(powder)/ ammonia	RT	10 min	8.05	2,160	116 at 0.05 A g ⁻¹	4
Zn(filings)/H ₂ SO ₄	RT	2 h	21.2	3,416	176	5
Zn(powder)/NaOH	RT	20 min	17.96	7,540	-----	2
Zn(powder)/ neutral solutions in the presence of EDTA*	RT	1 min Ultrasonic ation	33	14,200	-----	6
Zn(powder)/NaOH	RT	1 min Ultrasonic ation	31.2	13,500	-----	6
Zn(powder)/NaOH	RT	6 h	6.02		-----	7
Zn(powder)/NaOH	100	6 h	7.39		-----	7
Zn(powder)/HCl	RT	30 min	8.2	650	-----	8
Ni(powder)/HCl	RT	24 h			-----	9
Mg(ribbons)/HCl	RT	5 min		10.12	-----	10
NaBH ₄	RT	2 h	8.6	45	-----	11
Hydrazine hydrate	100	24 h	10.3	~200	-----	12

Solvothermal Sodium + ethanol	220	72 h	6.4	0.05	-----	13
HI	100	1h	12	298	-----	14
Hydrohalic acids	450	2 h	10.8	100,000	-----	15
Reduction with H ₂	35-40	72 h	5.9	43	-----	16
Yeast	80	2 h	5.6	0.783	-----	17
Polyethylene imine	95	-----	12.5	7,700	-----	18
Vitamin C	100	5 days	6.9	1,019	2.8	19
Isopropanol	100	5 days	30	4,600	35	19
Benzyl alcohol	RT	12 h	11.14		-----	20
Glycine	90	24 h	7.4	1,500	-----	21
P-phenylene diamine	RT	72 h	11.9		-----	22
Wild carrot	95	12 h	7.7	45	-----	23
Pyrrrole	90	1 h	9.7	1,122	-----	24
Hydroxyl amine	RT	48 h	-----	800	-----	24
L-ascorbic acid	50	3 h	6.1	8,650	152 at 1.5 A g-1	Current work

* EDTA refers Ethylenediaminetetraacetic acid and RT represents room temperature.

Table S2 Comparative electrochemical performances of various reduced GOs, surface modified graphene and graphene/conducting polymer composites

Materials	Specific capacitance	Charge-discharge cyclic stability/Retention	References
Zn reduced GO	116 F g ⁻¹ at 0.05 A g ⁻¹	-----	4
Zn reduced GO	176 F g ⁻¹	-----	5
Dimethyl ketoxime reduced GO	141 F g ⁻¹ at 3 A g ⁻¹	96% after 1500 cycles	25
Aqueous phytoextracts reduced GO	21(±2) F g ⁻¹ for ORGO, 18(±2) F g ⁻¹ for MRGO 17(±1.5) F g ⁻¹ for CRGO**	-----	26
Hydrazine monohydrate reduced GO	101 F g ⁻¹ at 20 mV s ⁻¹ 97 F g ⁻¹ at 400 mV s ⁻¹	-----	27
Annealing at 150 °C for 12 h	72 F g ⁻¹ at 5 A g ⁻¹	82% after 1500 cycles	28
Alcohols reduced GO	35 F g ⁻¹ at 25 mV s ⁻¹	-----	19
Thermally reduced GO	48 to 132 F g ⁻¹ at a scan rate of 0.5 to 0.01 V s ⁻¹	-----	29
Hydrazine reduced GO	133 F g ⁻¹ at 1 A g ⁻¹	-----	30
Electrochemically-reduced GO	128 F g ⁻¹	86% after 3500 cycles	31
Thermally exfoliated and reduced GO	117 F g ⁻¹ in aq. H ₂ SO ₄ 75 F g ⁻¹ in ionic liquid	-----	32
low-temperature (as low as 200 °C) reduced GO	122 F g ⁻¹ at 100 mA g ⁻¹	-----	33
9-anthracene carboxylic acid functionalized graphene	148 F g ⁻¹	-----	34
Sulfonated poly(ether-ether-ketone)	476 F g ⁻¹ at 6.6 A g ⁻¹	-----	35
KOH activated graphene sheets	136 F g ⁻¹ at 10 mVs ⁻¹	-----	36
Primary amine (Ethylene glycol)	187.6 F g ⁻¹ at 0.8 A g ⁻¹	60% after 1000 cycles	37
Reduced GO/polypyrrole composite	224 F g ⁻¹ at 240 Ag ⁻¹	83% after 5000 cycles	38
Multilayered nanoarchitecture of graphene nanosheets and	165 F g ⁻¹ at 1 A g ⁻¹	92% after 5000 cycles	39

polypyrrole nanowires			
Graphene-polypyrrole nanocomposite	267 F g ⁻¹ at 100 mV s ⁻¹	90% after 500 cycles	40
Sandwich-like polyaniline/graphene composite	377 F g ⁻¹ at 100 mV s ⁻¹	50.9 % after 1000 cycles	41
Electrophoretic deposition method to make the graphene nanosheets on nickel foam	100 F g ⁻¹ at 6 A g ⁻¹	61% after 700 cycles	42
Free-standing graphene/polyaniline nanofibers PSS-GS/PANi (10%)	301 F g ⁻¹	67% after 400 cycles	43
Sn-reduced GO at 50 °C	152 F g ⁻¹ at 1.5 A g ⁻¹	92% after 1500 cycles	Current work

**MRGO and ORGO represent *M. ferrea* Linn. leaf aqueous extract reduced GO and *C. sinensis* peel aqueous extract reduced GO, respectively. CRGO represents *C. esculenta* leaf aqueous extract reduced GO

References

1. Z. Fan, K. Wang, T. Wei, J. Yan, L. Song and B. Shao, *Carbon*, 2010, **48**, 1686-1689.
2. V.H. Pham, H.D. Pham, T. T. Dang, S. H. Hur, E. J. Kim, B. S. Kong, S. Kim and J. S. Chung, *J. Mater. Chem.*, 2012, **22**, 10530-10536.
3. Z. Fan, W. Kai, J. Yan, T. Wei, L.J. Zhi, J. Feng, Y. M. Ren, L. P. Song and F. Wei, *ACS Nano*, 2011, **5**, 191-198
4. Y. Liu, Y. Li, M. Zhong, Y. Yang, Y. Wen, M. Wang. *J. Mater. Chem.*, 2011, **21**, 15449-15455.
5. R. S. Dey, S. Hajra, R. K. Sahu, C. R. Raj and M. K. Panigrahi, *Chem. Commun.*, 2012, **48**, 1787-1789.
6. X. Mei, H. Zheng and J. Ouyang, *J. Mater. Chem.*, 2012, **22**, 9109-9116.
7. S. Yang, W. Yue, D. Huang, C. Chen, H. Lin and X. Yang, *RSC Advances*, 2012, **2**, 8827-8832.
8. P. Liu, Y. Huang and L. Wang, *Materials Letters*, 2013, **91**, 125-128

9. R. Krishna, E. Titus, L. C. Costa, J. C. J. M. D. S. Menezes, M. R. P. Correia, S. Pinto, J. Ventura, J. P. Araujo, J. A. S. Cavaleiro and J. J. A. Gracio, *J. Mater. Chem.*, 2012, **22**, 10457-10459.
10. B. K. Barman, P. Mahanandia, and K. K. Nanda, *RSC Adv.*, 2013, **3**, 12621-12624.
11. H.-J. Shin, K. K. Kim, A. Benaya, S.-M. Yoon, H. K. Park, I.-S. Jung, M. H. Jin, H.-K. Jeong, J. M. Kim, J.-Y. Choi, and Y. H. Lee, *Adv. Func. Mater.* 2009, **19**, 1987-1992.
12. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2007, **45**, 1558-1565.
13. M. Choucair, P. Thordarson and J. A. Stride, *Nat. Nanotechnol.* 2009, **4**, 30-33.
14. S. Pei, J. Zhao, J. Du, W. Ren and H.-M. Cheng, *Carbon*, 2010, **48**, 4466-4474.
15. Z.-S. Wu, W. Ren, L. Gao, B. Liu, C. Jiang, H.-M. Cheng, *Carbon*, 2009, **47**, 493-499.
16. P. Khanra, T. Kuila, N. H. Kim, S. H. Bae, D.-S. Yu and J. H. Lee, *Chem. Eng. J.* 2012, **183**, 526- 533.
17. H. Liu, T. Kuila, N. H. Kim, B.-C. Ku and J. H. Lee, *J. Mater. Chem. A*, 2013, **1**, 3739-3746.
18. M. J. F. Merino, L. Guardia, J. I. Paredes, S. V. Rodil, P. S. Fernandez, A. M. Alonso, and J. M. D. Tascon, *J. Phys. Chem. C*, 2010, **114**, 6426-6432.
19. D. R. Dreyer, S. Murali, Y. Zhu, R. S. Ruoff and C. W. Bielawski, *J. Mater. Chem.*, 2011, **21**, 3443-3447.
20. S. Bose, T. Kuila, A. K. Mishra, N. H. Kim and J. H. Lee, *J. Mater. Chem.*, 2012, **22**, 9696-9703.
21. Y. Chen, X. Zhang, P. Yu and Y. Ma, *Chem. Commun.*, 2009, 4527-4529.
22. T. Kuila, S. Bose, P. Khanra, A. K. Mishra, N. H. Kim and J. H. Lee, *Carbon*, 2012, **50**, 914-921.
23. C. A. Amarnath, C. E. Hong, N. H. Kim, B.-C. Ku and T. Kuila and J. H. Lee, *Carbon*, 2011, **49**, 3497-3502.
24. X. Zhou, J. Zhang, H. Wu, H. Yang, J. Zhang and S. Guo, *J. Phys. Chem. C*, 2011, **115**, 11957-11961.
25. P. Su, H.-L. Guo, L. Tian and S.-K. Ning, *Carbon* 2012, **50**, 5351-5358.
26. S. Thakur and N. Karak, *Carbon*, 2012, **50**, 5331-5339.

27. M. D. Stoller, S. Park, Y. Zhu, J. An, and Rodney S. Ruoff, *Nano Lett.*, 2008, **8**, 3498-3502.
28. K. Ku, B. Kim, H. Chung and W. Kim, *Synthetic Met.*, 2010, **160**, 2613-2617.
29. L. T. Le, M. H. Ervin, H. Qiu, B. E. Fuchs and W. Y. Lee, *Electrochem. Commun.*, 2011, **13**, 355-358.
30. N. Xiao, D. Lau, W. Shi, J. Zhu, X. Dong, H. H. Hng and Q. Yan, *Carbon*, 2013, **57**, 184-190.
31. X.-Y. Peng, X.-X. Liu, D. Diamond and K. T. Lau, *Carbon*, 2011, **49**, 3488-3496.
32. S. R. C. vivekchand, C. S. Rout, K. S. Subrahmanyam, A. Govindaraj and C. N. R. Rao, *J. Chem. Sci.*, 2008, **120**, 9-13.
33. W. Lv, D.-M. Tang, Y.-B. He, C.-H. You, Z.-Q. Shi, X.-C. Chen, C.-M. Chen, P.-X. Hou, C. Liu and Q.-H. Yang, *ACS Nano*, 2009, **3**, 3730-3736.
34. S. Bose, T. Kuila, A. K. Mishra, N. H. Kim and J. H. Lee, *Nanotechnology*, 2011, **22**, 405603.
35. T. Kuila, A. K. Mishra, P. Khanra, N. H. Kim, M. E. Uddin and J. H. Lee, *Langmuir*, 2012, **28**, 9825-9833.
36. Y. Li, M. v. Zijll, S. Chiang and N. Pan, *J. Power Sources*, 2011, **196**, 6003-6006.
37. L. Lai, L. Chen, D. Zhan, L. Sun, J. Liu, S. H. Lim, C. K. Poh, Z. Shen, J. Lin, *Carbon*, 2011, **49**, 3250-3257.
38. J. Wang, Y. Xu, J. Zhu and P. Ren, *J. Power Sources*, 2012, **208**, 138-143.
39. S. Biswas and L. T. Drzal, *Chem. Mater.*, 2010, **22**, 5667-5671.
40. S. Bose, N. H. Kim, T. Kuila, K.-T. Lau and J. H. Lee, *Nanotechnology* 2011, **22**, 295202.
41. Y. Li, H. Peng, G. Li and K. Chen, *Eur. Polym. J.* 2012, **48**, 1406-1412.
42. J. Yan, T. Wei, Z. n Fan, W. Qian, M. Zhang, X. Shen and F. Wei, *J. Power Sources*, 2010, **195**, 3041-3045.
43. S. Liu, X. Liu, Z. Li, S. Yang and J. Wang, *New J. Chem.*, 2011, **35**, 369-374.