

Electrochemical properties

Cyclic voltammetry and galvanostatic charge-discharge were carried out with a three-electrode system from 0 to 1 V in 1 M H₂SO₄ solution to test the electrochemical performance of the as-obtained rGO. **Figure 8** showed that with the scanning rate increasing from 5 to 100 mV s⁻¹, all CV curves of rGO electrode exhibited the same shape, however, area covered by them increased, which proved its good capacitance behavior and rate capability. On the other hand, no redox peaks were observed throughout the scan region, signaling the typicality of the EDLC for carbon-based materials [1,14].

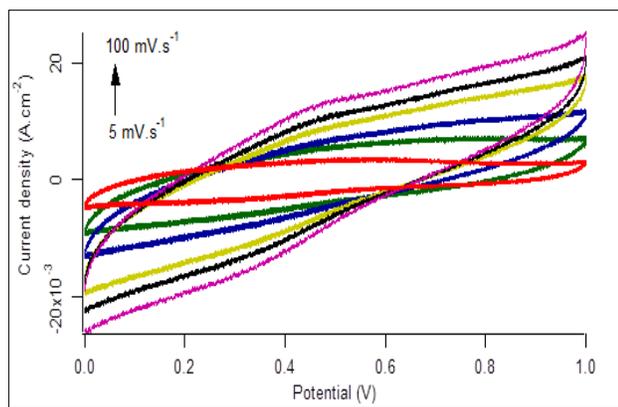


Figure 8. CV curves of rGO at different scan rates (three-electrode system).

Figure 9 presents the charge-discharge curves of rGO electrode at various current densities from 1 to 5 A g⁻¹. These charge-discharge curves show triangular forms, which are symmetric and rather slope proving good capacitive quality of rGO electrode. Based on **Figure 9** and the abovementioned equation (1), at the current density of 1 A g⁻¹, the SC value of rGO electrode can be determined, 262 F g⁻¹.

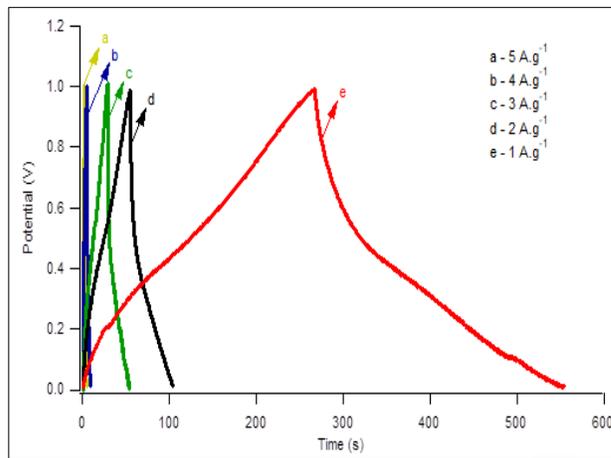


Figure 9. Galvanostatic charge-discharge curves of rGO at different current densities.

Figure 10a demonstrates its different charge-discharge cycles at the fixed current density of 1 A g⁻¹. Obtained graph illustrates series of isosceles triangle curves, which is reasonable with CV behavior of rGO and suggesting that its capacitance can maintain well. **Table 1** shows the comparison of SC of rGO electrode with reported values.

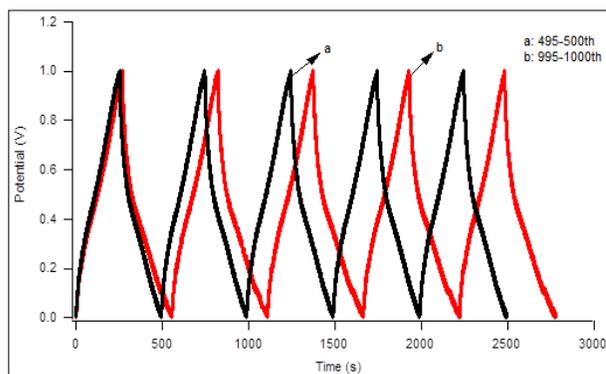


Figure 10a. The different cycles of rGO at 1 A g⁻¹.

Table 1. Comparison of electrochemical performances in terms of specific capacitance of various rGO electrodes.

Sample	Electrode	Current density (A g ⁻¹)	Specific capacitance (F g ⁻¹)	Electrolyte	References
EdoX-GO	rGO	1.0	255	6.0 M KOH	[42]
Graphene	Graphene nanosheets	0.5	272	1.0 M H ₂ SO ₄	[23]
GMs	Graphene	0.5	205	30% KOH	[43]
HRGO	rGO	1.0	128	0.1 M Na ₂ SO ₄	[13]
rGO	rGO	1.3	137	1.0 M H ₂ SO ₄	[39]
rGO	rGO	1.0	262	1.0 M H ₂ SO ₄	This work

In comparison with some previous works, it seems clear that rGO has a comparable SC value [23,42] and even much higher than that of HRGO - 128 F g^{-1} [13], rGO - 137 F g^{-1} [39] or rGO - 205 F g^{-1} [43]. Another experiment to reassure about electrochemical stability of rGO electrode is cycling measurement. Still at the fixed current density of 1 A g^{-1} , **Figure 10b** displays the changes of Coulombic efficiency throughout 1000 continuous cycles in the potential range of 0 to 1 V. It is obvious that the SC of rGO electrode shows no significant change after 40 cycles, however, quickly increases to 242 F g^{-1} up to 135 cycles. And then, it slightly increases and reaches the maximum value of 262 F g^{-1} after 400 cycles. Based on the results from the galvanostatic charge-discharge graph, Coulombic efficiency could be calculated by applying equation (2). After 400 charge-discharge cycles are conducted, the SC initiates to slightly decrease and preserves at approximate 90% of the initial value, confirming good electrochemical cyclic stability in consecutive charge-discharge cycles.

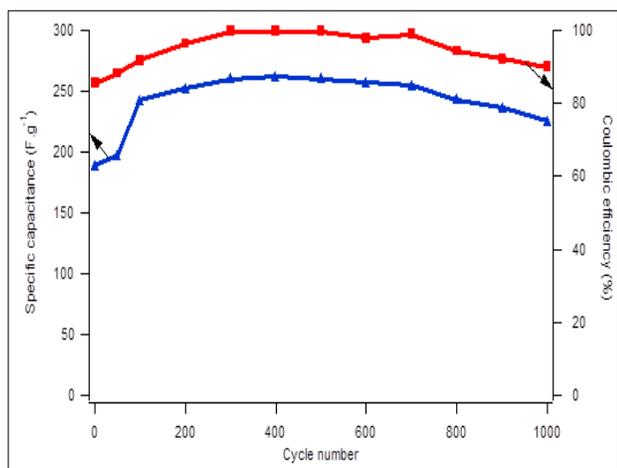


Figure 10b. Charge-discharge cyclic stability of rGO up to 1000 cycles, at a current density of 1 A g^{-1} .

CONCLUSION

To sum up, we introduce the green, easy, and low-cost chemical way utilizing shikimic acid as reducing reagent to fabricate rGO nanosheets, opening up the possibilities in mass production of rGO. The as-prepared rGO was characterized by various physicochemical and electrochemical measurements. The obtained result demonstrates that in $1 \text{ M H}_2\text{SO}_4$ electrolyte solution, at the current density of 1 A g^{-1} , the as-synthesized graphene nanosheets exhibit high SC value (262 F g^{-1}). Besides, after completing 1000 charge-discharge cycles, the SC can retain nearly 90%, showing long-term cyclability. In addition, its high power density makes rGO an ideal electrode material for energy storage application.

HIGHLIGHTS

- Graphene oxide was reduced by shikimic acid, an eco-friendly reagent.
- The reduction of the graphene oxide nanosheets was confirmed by various characterization methods.
- The obtained reduced graphene oxide is few layer nanosheets.
- The as-synthesized rGO exhibits high SC value and long-term cyclability.

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REFERENCES

1. Yang W, Gao Z, Wang J, Wang B, Liu Q, et al. (2012) Synthesis of reduced graphene nanosheet/urchin-like manganese dioxide composite and high performance as supercapacitor electrode. *Electrochimica Acta* 69: 112-119.
2. Simon P, Gogotsi Y (2008) Materials for electrochemical capacitors. *Nat Mater* 7: 845-854.
3. Zhang LL, Zhao XS (2009) Carbon-based materials as supercapacitor electrodes. *Chem Soc Rev* 38: 2520-2531.
4. Liu C, Li F, Ma LP, Cheng HM (2010) Advanced materials for energy storage. *Adv Mater* 2: E28-E62.
5. Nyholm L, Nystrom G, Mihranyan A, Maria Strømme (2011) Towards flexible polymer and paper-based energy storage devices. *Adv Mater* 23: 3751-3769.
6. Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, et al. (2004) Electric field effect in atomically thin carbon films. *Science* 306: 666-669.
7. Geim AK, Novoselov KS (2007) The rise of graphene. *Nat Mater* 6: 183-191.
8. Li D, Mueller MB, Gilje S, Kaner RB, Wallace GG (2008) Processable aqueous dispersions of graphene nanosheets. *Nat Nanotechnol* 3: 101-105.
9. Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ, et al. (2006) Graphene-based composite materials. *Nature* 442: 282-286.
10. Ke Q, Wang J (2016) Graphene-based materials for supercapacitor electrodes - A review. *J Materiomics* 2: 37-54.

11. Marcelina V, Syakir N, Wyantuti S, et al. (2017) Characteristic of thermally reduced graphene oxide as supercapacitors electrode materials. IOP Conference Series: Material Science and Engineering 196: 012034.
12. Martinez JG, Otero TF, Bosch-Navarro C, Coronado E, Mart-Gastaldo C, et al. (2012) Graphene electrochemical responses sense surroundings. *Electrochimica Acta* 81: 49-57.
13. Wang C, Zhou J, Du F (2016) Synthesis of highly reduced graphene oxide for supercapacitor. *J Nanomater* 2016: 1-7.
14. Karthika P, Rajalakshmi N, Dhathathreyan K (2012) Functionalized exfoliated graphene oxide as supercapacitor electrodes. *Soft Nanosci Lett* 2: 59-66.
15. Liu Y, Zhang Y, Ma G, Wang Z, Liu K, et al. (2013) Ethylene glycol reduced graphene oxide/polypyrrole composite for supercapacitor. *Electrochimica Acta* 88: 519-525.
16. Zhu P, Shen M, Xiao S, Zhang D (2011) Experimental study on the reducibility of graphene oxide by hydrazine hydrate. *Physica B* 406: 498-502.
17. Park S, An J, Potts JR (2011) Hydrazine-reduction of graphite- and graphene oxide. *Carbon* 49: 3019-3023.
18. Zhu C, Guo S, Fang Y, Dong S (2010) Reducing sugar: New functional molecules for the green synthesis of graphene nanosheets. *ACS Nano* 4: 2429-2437.
19. Akhavan O, Ghaderi E, Aghayee S, Fereydoonia Y, Talebi A (2012) The use of a glucose-reduced graphene oxide suspension for photothermal cancer therapy. *J Mater Chem* 27: 13773-13781.
20. Zhang J, Yang H, Shen G, Cheng P, Zhang J, et al. (2010) Reduction of graphene oxide via L-ascorbic acid. *Chem Commun* 46: 1112-1114.
21. Fernández-Merino MJ, Guardia L, Paredes JI, Villar-Rodil S, Fernandez PS, et al. (2010) Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions. *J Phys Chem C* 114: 6426-6432.
22. Gao J, Liu F, Liu Y, Ma N, Wang Z, et al. (2010) Environment-friendly method to produce graphene that employs vitamin C and amino acid. *Chem Mater* 22: 2213-2218.
23. Xing B, Yuan R, Zhang C, Huang G, Guo H, et al. (2017) Facile synthesis of graphene nanosheets from humic acid for supercapacitors. *Fuel Process Technol* 65: 112-122.
24. Vu THT, Tran TTT, Le HNT, Nguyen PHT, Bui NQ, et al. (2015) A new green approach for the reduction of graphene oxide nanosheets using caffeine. *Bull Mater Sci* 38: 667-671.
25. Akhavan O, Kalae M, Alavi ZS, Esfandiari A, Ghiasi SMA (2012) Increasing the antioxidant activity of green tea polyphenols in the presence of iron for the reduction of graphene oxide. *Carbon* 50: 3015-3025.
26. Akhavan O, Ghaderi E (2010) Escherichia coli bacteria reduce graphene oxide to bactericidal graphene in a self-limiting manner. *Carbon* 50: 1853-1860.
27. Salas EC, Sun Z, Luttge A, Tour JM (2010) Reduction of graphene oxide via bacterial respiration. *ACS Nano* 4: 852-856.
28. Cardoso SF, Lopes LMX, Nascimento IR (2014) Eichhornia crassipes: An advantageous source of shikimic acid. *Rev Bras Farmacogn* 24: 439-442.
29. Ghosh S, Chisti Y, Banerjee UC (2012) Production of shikimic acid. *Biotechnol Adv* 30: 1425-1431.
30. Enrich LB, Scheuermann ML, Mohadjer A, Matthias KR, Eller CF, et al. (2008) *Liquidambar styraciflua*: A renewable source of shikimic acid. *Tetrahedron Lett* 49: 2503-2505.
31. Cai M, Luo Y, Chen J, Liang H, Sun P, et al. (2014) Optimization and comparison of ultrasound-assisted extraction and microwave-assisted extraction of shikimic acid from Chinese star anise. *Sep Purif Technol* 133: 375-379.
32. Rawat G, Tripathi P, Saxena RK (2013) Expanding horizons of shikimic acid. Recent progresses in production and its endless frontiers in application and market trends. *Appl Microbiol Biotechnol* 97:4277-4287.
33. Tran DNH, Kabiri S, Losic D (2014) A green approach for the reduction of graphene oxide nanosheets using non-aromatic amino acids. *Carbon* 76: 193-202.
34. Ang PK, Wang S, Bao Q, Thong JT, Loh KP (2009) High-throughput synthesis of graphene by intercalation-exfoliation of graphite oxide and study of ionic screening in graphene transistor. *ACS Nano* 3: 3587-3594.
35. Qiu JD, Wang GC, Liang RP, Xia XH, Yu HW, et al. (2011) Controllable deposition of platinum nanoparticles on graphene as an electrocatalyst for direct methanol fuel cells. *J Phys Chem* 115: 15639-15645.
36. Stankovich S, Dikin DA, Piner RD, Kolhaas KA, Kleinhammes A, et al. (2007) Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* 45: 1558-1565.

37. Tuinstra F, Koenig J (1970) Raman spectrum of graphite. J Phys Chem 53: 1126.
38. Kudin KN, Ozbas B, Schniepp HC, Prud'homme RK, Aksay IA, et al. (2007) Raman spectra of graphite oxide and functionalized graphene sheets. Nano Lett 8: 36-41.
39. Jana M, Saha S, Khanra P, Murmu NC, Srivastava SK, et al. (2014) Bio-reduction of graphene oxide using drained water from soaked mung beans (*Phaseolus aureus* L.) and its application as energy storage electrode material. Mater Sci Eng 186: 33-40.
40. Garrigues JM, Bouhsain Z, Garrigues S, de la Guardia M (2000) Fourier transform infrared determination of caffeine in roasted coffee samples. Fresenius J Anal Chem 366: 319-322.
41. Kuila T, Bose S, Khanra P, Mishra AK, Kim NH, et al. (2012) A green approach for the reduction of graphene oxide by wild carrot root. Carbon 50: 914-921.
42. Abdelkader AM (2015) Electrochemical synthesis of highly corrugated graphene sheets for high performance supercapacitors. J Mater Chem 3: 8519-8525.
43. Wang Y, Shi Z, Huang Y, Ma Y, Wang C, et al. (2009) Supercapacitor devices based on graphene materials. J Phys Chem C 113: 13103-13107.