

Scientific paper

Facile Preparation of Graphene by High-temperature Electrolysis and its Application in Supercapacitor

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Abstract

Graphene is well known owing to its astonishing properties: stronger than diamond, more conductive than copper and more flexible than rubber. Because of its potential uses in industry, researchers have been searching for less toxicity ways to make graphene in large amount with lower cost. We demonstrated an efficient method to prepare graphene by high temperature electrolysis technique. High resolution scanning electron microscopy and raman spectroscopy were used to characterize the microstructure of graphene. Graphene was assembled into the supercapacitor and its performance of electrochemical capacitor was investigated by constant current charge and discharge, cyclic voltammetry and AC impedance. The results showed that the micro-morphology of the prepared graphene was multilayer and it was favorable when the electrolytic voltage was 1.5 V. When the current density is 1 mA/cm², the specific capacitance of the graphene supercapacitor can reach 78.01 F/g in 6 mol/L KOH electrolyte, which was an increase of 114% compared with 36.43 F/g of conventional KOH electrolyte.

Keywords: Graphene, Supercapacitor, High temperature electrolysis

1. Introduction

Graphene, a single graphite layer or the single-atom-thick carbon, is a hexagonal honeycomb two-dimensional grid structure which composes of carbon atoms by sp² hybridization. Graphite is currently the world's thinnest nanomaterials, and its thickness is only 0.335 nm. In 2004, two scientists of the University of Manchester Andre Geim and Konstantin Novoselov found graphene,¹ which resulted in the acquisition of the 2010 Nobel Prize in physics. Graphite has attracted huge interests for its remarkable properties such as large specific surface area, high electrical conductivity and great stiffness.^{2–7} In Feb, 2014, it was just reported by Nature.com that graphene conducts electricity ten times better than expected and carbon layers grown on silicon carbide conduct electricity even better than the theory predicted. The finding could help graphene realize its promise in high-end electronics, where researchers have long hoped it could outperform traditional materials such as silicon. Early Graphene results were limited to academic research but increasingly

industry giants are in the running. To meet the burst market of graphene, it is always a very interesting topic to find and establish simple and cost-saving method to prepare graphene.

The first reported preparation of graphene was by Novoselov and Gaim in 2004 by exfoliation using a simple adhesive tape. The exfoliation methods have the advantage of providing graphene of very high quality and purity, and, due to the low complexity, they are perfect for laboratory research. The size of the obtained flakes, however, as well as the controllability are too poor for industrial production. In the manufacturing methods of graphene so far, the micro mechanical stripping method can not reliably produce large-scale graphene;^{8,9} Epitaxial growth approach requires the use of expensive rare metals, high cost, and the harsh reaction conditions, high requirements for equipment;^{10,11,17} Chemical vapor deposition method although can meet the requirement of the preparation of high quality graphene,^{12,13} but the process is complex, and the yield is low, so it is not suitable for mass production. In detail, CVD is a method to produce high

quality graphene in large volume that manufactures graphene on the board of metal film that serves as a catalyst. It manufactures the material by blowing out gas called the source gas onto the board. This method requires intensive post-processing (transfer process) as it has to remove used metal after the manufacturing process and move the manufactured graphene to another board such as a solar cell substrate. In this process the quality quickly degrades as it is prone to wrinkles or cracks. Oxidation-reduction method has a series of merits such as high yield, low cost, but in this method will produce a lot of waste liquid which could pollute the environment;^{14–16} For the solvothermal synthesis, Graphene sheets are obtained through solvothermal reduction of colloidal dispersion of graphene oxide in benzyl alcohol.¹⁸ The reduction of graphene oxidation (GO) is carried out by chemical methods, using different reductants such as hydrazine, dimethylhydrazine, hydroquinone, NaBH_4 , and usually the reductants are hazardous.¹⁹ To achieve a wide range of applications in many fields, the key issues need to be addressed is how to prepare high-quality graphene with simple, rapid and low-cost methods. Herein, we demonstrate a new technology to prepare graphene by high-temperature electrolysis using CaCO_3 (the primary component of limestone).

Limestone is abundant on the earth, and the price is very low (the lowest price found on line is 80 \$ per ton in United States and 50 \$ per ton in China). Therefore, this presented work used CaCO_3 (the major component of limestone) as raw material and the graphene with excellent performance was made through electrolyzing molten carbonate in the condition of high-temperature. The method has strong operability with low cost. This work as a new type of preparation technology is anticipated to open a possibility for graphene green environmental protection and is therefore suitable for industrial production.

2. Experimental

2. 1. Reagents

Calcium carbonate (CaCO_3 , AR) and Lithium carbonate (Li_2CO_3 , AR) were purchased from Tianjing reagent factory (Tianjing, China). Hydrochloric acid (HCl, AR) was purchased from Hebei Chemical Company (Hebei, China). High purity nickel (Ni, 99.99%) was obtained from Jiangsu Chemical Company (Jiangsu, China)

2. 2. Instrumentation

ZEISS SUPRA55 thermal field emission scanning electron microscope (Zeiss, Germany) was used to measure the micro-morphology of the sample; LabRAM HR 800 type high resolution Raman spectrometer (HORIBA Jobin Yvon, France) with laser wavelength of 633nm at the wavenumber range of $1000\text{--}3000\text{cm}^{-1}$ was applied to

record the Raman spectra of graphene. Cyclic voltammetry, AC impedance and constant current charge and discharge tests were performed in the German Zahner Zenium electrochemical workstation. The specific test methods are as follows: Voltages of Cyclic voltammetry and galvanostatic charge-discharge were 0–0.8V, the specific capacitance is calculated according to equation:

$$C_p = 2I\Delta t / (m\Delta U) \quad (1)$$

Where C_p is the specific capacitance of the required electrode material in $\text{F} \cdot \text{g}^{-1}$; I is the discharge current in A; Δt is the discharge time in s; m is the mass of active material in a single electrode film in g; ΔU is the working potential window when the electrode discharging in V. The frequency range that was tested by AC impedance was $0.01\text{--}1 \times 10^5$ Hz, and amplitude of sine wave was 5 mV.

2. 3. Procedures

2. 3. 1. Preparation of Graphene

Firstly, 12 g calcium carbonate and 20 g lithium carbonate were put into the crucible after uniformly grinding and mixing, with stainless steel as the cathode of electrolytic reaction and nickel sheet as the anode. Secondly, connecting the electrode wire and covering the crucible outlet with asbestos net, the system was placed into muffle furnace. Thirdly, the muffle furnace was adjusted to 750 °C and applied to the the different bipolar voltage of the crucible between 1.5 and 3.5V. The timer was turned on after the furnace temperature reached 750 °C. The reaction system were taken out 5 hours and cooled down to room temperature naturally. The product in the crucible was washed with 6mol/L HCl until no bubble was observed and then washed with distilled water repeatedly until the supernatant was centrifuged at neutral pH. Finally, the product was dried in an air-dry oven at 60 °C and the black graphene powder was obtained.

2. 3. 2. Preparation of the Super Capacitor Electrode

Graphene, conductive acetylene black and PTFE binder with the mass ratio of 8:1:1 were stirred uniformly and added a certain amount of anhydrous ethanol. The mixture was ground into rubber pulpy in a glass mortar. The pulpy was rolled repeatedly in a roller press to a thickness of 0.2 mm and was dried in a vacuum drying oven at 80 °C. The obtained material was cut into electrode plate with the diameter of 1 cm. Two electrodes that had the same quality (difference is less than 0.5 mg) were saturated in vacuum for 90 min in 6 mol/L KOH electrolyte. The polypropylene film as the diaphragm and 6 mol/L KOH as electrolyte were putted into the stainless steel mold according to the order of electrode piece – diaphragm – electrode piece and assembled into sandwich-

type, symmetrical-type super capacitor. The electrochemical performance was tested. Results and discussion

2. 3. 3. Characterization of Graphene by SEM: Microstructure of Sample can be Controlled by the Electrolysis Voltage

The samples prepared in the different voltage between 1.5 V and 3.5 V were examined by high resolution scanning electron microscope and the results were shown in Fig. 1. Wherein, the micro morphology of samples prepared at higher voltage (shown in Fig. 1a, b, c) were rod-like, indicating that graphene were not formed under these conditions. The sample prepared at lower voltage (shown

in Fig. 1d and 1e) showed clearly that graphene with preferable morphology was obtained, which was exactly the type of translucent silk yarn. The results illustrated that graphene can be obtained only when the electrolysis voltage was lower than 2.0 V in the high temperature electrolysis method.

2. 3. 4. Characterization of Graphene by Raman Spectroscopy

Raman spectroscopy, an effective and non-destructive tool, is used to characterize the structures and properties of carbon nano materials. The Raman spectra of the Graphene that was prepared with the electrolysis voltage

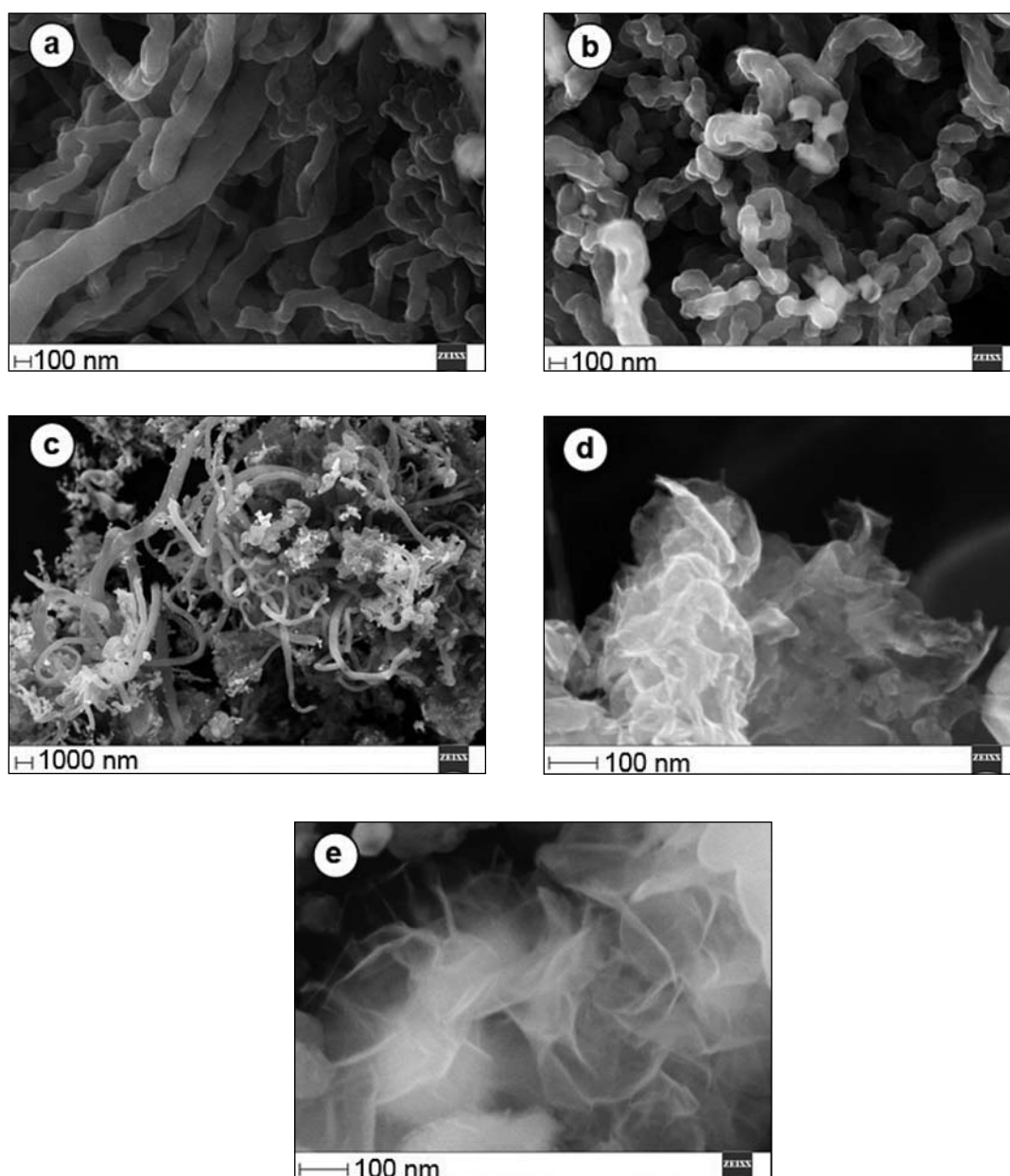


Fig. 1. SEM images of graphene that were prepared under different electrolysis voltages: (a) 3.5 V, (b) 3.0 V, (c) 2.5 V, (d) 2.0 V and (e) 1.5V

1.5 V was shown in Fig. 2. Graphene can be identified by the position and shape of its G and G' peaks. The G peak that appears in the vicinity of 1584cm^{-1} is caused by the tensile telecontrol of carbon rings or sp^2 hybrid structure of atomic in long-chain, and represents the ordered structure of sp^2 bond; The D peak appears around 1327cm^{-1} is associated with the structure of sp^3 hybridization, and delegates the defects and amorphous structure that are located on the edge of the graphene; The G' peak involves double phonon scattering and appears around 2648cm^{-1} , indicating that the graphene that was prepared by this method was multilayer graphene.

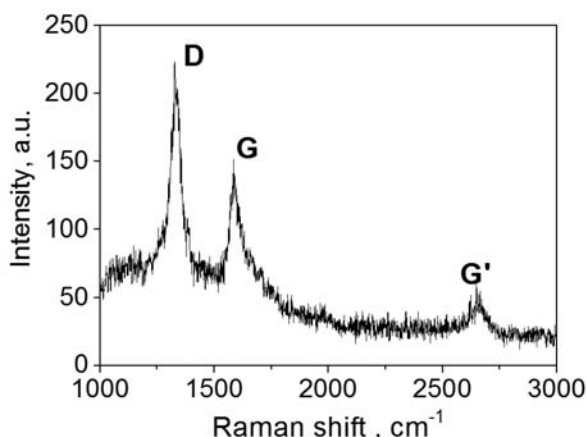


Fig. 2. Raman spectra of graphene with 1.5 V electrolysis voltage.

2. 3. 5. Electrochemical Properties of Graphene as Prepared

Constant current charge-discharge curves of graphene that were prepared with the electrolysis voltage 1.5 V and the different current densities as a function of time were shown in Fig. 3. It is apparent that the four curves are all typical triangular symmetry structures and the vol-

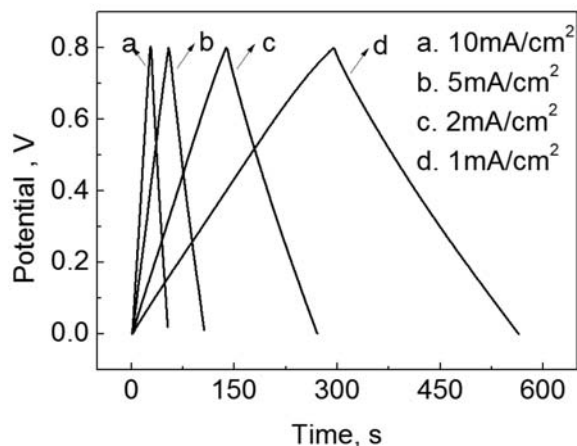


Fig. 3. Galvanostatic charge/discharge curves of graphene at different current density.

tage drop is not observable. The results revealed that the charge-discharge process was the standard electric double layer capacitor and the resistance of electrode material was small. The corresponding sizes of the specific capacitance, which were calculated according to equation 2, are listed in Table 1.

$$C = I/[(dE/dt) \times m] \approx I/[(\Delta E/\Delta t) \times m] \quad (2)$$

where I is the constant discharging current, dE/dt indicates the slope of the discharge plot of the discharging curves, and m is the mass of the corresponding electrode materials measured. It can be seen from the table that the material specific capacitance value shows a decreasing trend with the increase of current density. The reason is that the charge does not timely and fully spread into the hole of the material when large current charges and discharges. However, the specific capacitance decreases only 2.77% when the current density increased 10 times, which shows that graphene prepared in the method has good capacitance performance and rate capability when the large current charges and discharges.

Table 1. The specific capacitance of graphene at different current density based on equation 1

	I(mA)	$\Delta U(V)$	$\Delta t(s)$	m(g)	Cp(F/g)
a	7.85	0.7915	26.0	0.0068	75.84
b	3.93	0.7927	52.4	0.0068	76.31
c	1.57	0.7989	132.4	0.0068	76.53

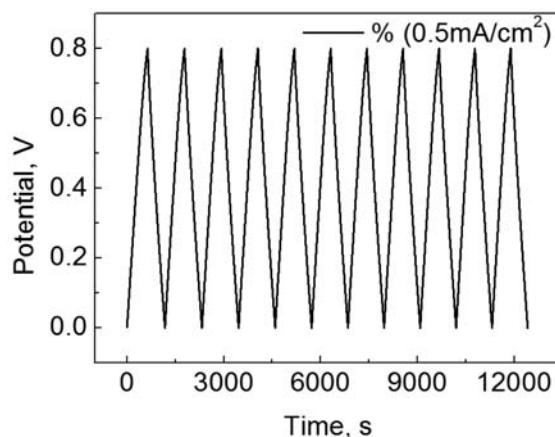


Fig. 4. Galvanostatic charge/discharge curves of graphene at a current density of 0.5 mA/cm^2

Fig. 4 is the constant current charge-discharge curve of the graphene that was prepared with the electrolysis voltage 1.5 V and 0.5 mA/cm^2 current density. It is obvious that the charge-discharge curve of graphene is still symmetrical triangle after charging and discharging repeatedly, which illustrates and confirms that graphene as prepared has good

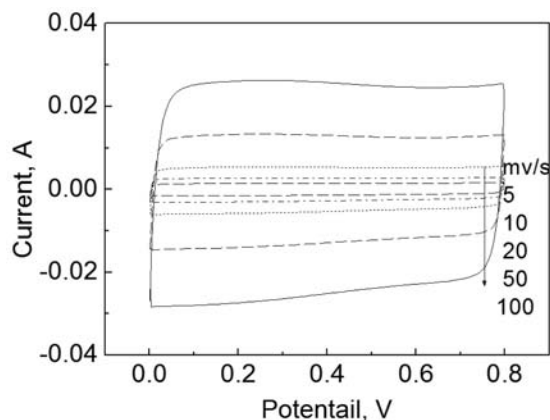


Fig. 5. Cyclic voltammetry curves of graphene at different scanning rates (mv/s).

capacitance property and cycle stability. Cyclic voltammetry curves of graphene that were prepared with the electrolysis voltage 1.5 V with different scan rates were shown in Fig. 5. It can be seen from the diagram that the CV curve of graphene is smooth and redox peak doesn't emerge, which shows that there is only the electric double layer capacitance, and no Faraday capacitance. The CV curve shows a standard rectangular and is a typical cyclic voltammetry curve of electric double layer capacitor. With increasing the scan rate, rectangular showed a certain degree of distortion. This is because the ions can not timely enter the smaller pores of the graphene surface and result in dispersion capacitance phenomenon in high scan rates. However, the graphic still remains good symmetry, indicating that material had excellent performance of reversible cycling.

AC impedance of the graphene that was prepared with the electrolysis voltage 1.5 V was investigated and shown in Fig. 6. The curve is a straight line that is parallel to the x-axis in the high frequency area and it is not the usual semi-circular arc, indicating that charge transfer resistance of the material is very small. Through the intersection of the real axis and the highest impedance of the impedance curve can be estimated that resistance of the

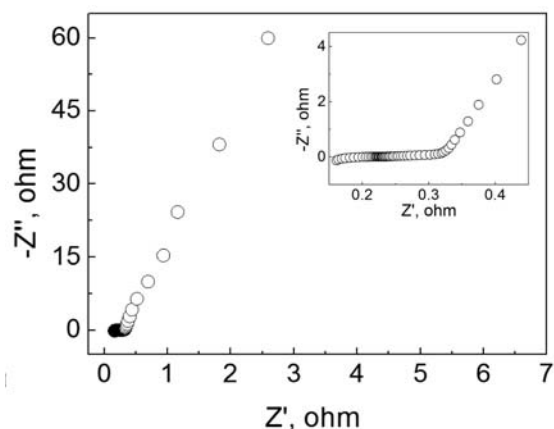


Fig. 6. Electrochemical impedance spectra of graphene.

electrode is 0.1610Ω . Curve is a straight line that is approximately 45° in the intermediate frequency area, known as the Warburg impedance, which is caused by diffusion and transfer of ion; in the low frequency area, curve is a straight line that is approximately 90° , which represents that graphene has ideal capacitance behavior.

3. Conclusions

The graphene with better microstructure has been synthesized by high temperature electrolysis method, in which the reaction temperature is 750°C , the electrolysis voltage is 1.5 V, and mass ratio of the calcium carbonate and lithium carbonate is 3:5. The specific capacitance of graphene can reach 78.01 F/g in the 6 mol/L KOH electrolyte when the current density is 1 mA/cm^2 . In summary, this method has the advantage of providing graphene of very high quality and purity, and, due to the low complexity, they are perfect for both laboratory research and industrial production.

4. References

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science*. **2004**, 306(5696), 666–669.
2. Y. B. Zhang, Y. W. Tan, H. L. Stormer, P. Kim, *Nature*. **2005**, 438(7065), 201–204.
3. Q. H. Yang, W. Lu, Y. G. Yang, M. Z. Wang, *New Carbon Materials*. **2008**, 23(2), 97–103.
4. J. Baringhaus, M. Ruan, F. Edler, A. Tejada, M. Sicot, A. Taleb-Ibrahimi, A. P. Li, Z. G. Jiang, E. H. Conrad, C. Berger, C. Tegenkamp, W. A. de Heer, *Nature*, **2014**, 506(7488), 349–354.
5. L. S. Schadler, S. C. Giannaris, P. M. Ajayan, *Applied Physics Letters*. **1998**, 73(26), 3842–3884.
6. A. K. Geim, *Science*. **2009**, 324(5934), 1530–1534.
7. L. J. Zhi, Y. Fang, F. Y. Kang, *New Carbon Materials*. **2011**, 26(26), 5–8.
8. F. Y. Kang, Y. B. He, B. H. Li, H. D. Du, *New Carbon Materials*. **2011**, 26(3), 246–254.
9. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, V. Grigorieva, S. V. Dubonos, A. A. Firsov, *Nature*. **2005**, 438(7065), 197–200.
10. K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A. K. Geim, *PNAS*. **2005**, 102(30), 10451–10453.
11. C. Berger, Z. M. Song, X. B. Li, X. S. Wu, N. Brown, C. Naud, D. Mayou, T. B. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, W. A. de Heer, *Science*. **2006**, 312(5777), 1191–1196.
12. T. Seyller, A. Bostwick, K. V. Emtsev, K. Horn, L. Ley, J. L. McChesney, T. Ohta, J. D. Riley, E. Rotenberg, F. Speck, *Phys Status Solidi (B)*. **2008**, 245(7), 1436–1446.

13. C. A. Di, D. C. Wei, G. Yu, Y. Q. Liu, Y. L. Guo, D. B. Zhu, *Advanced Materials*. **2008**, 20(17), 3289–3293.
14. C. D. Liao, Y. Y. Lu, S. R. Tamalampudi, H. C. Cheng, Y. T. Chen, *J. Phys. Chem. A*. **2013**, 117(39), 9454–9461.
15. S. Park, R. S. Ruoff, *Nature nanotechnology*. **2009**, 4(4), 217–224.
16. M. J. McAllister, J. L. Lio, D. H. Adamson, H. C. Schniepp, A. A. Abdala, J. Liu, M. Herrera-Alonso, D. L. Milius, R. Car, R. K. Prudhomme, I. A. Aksay, *Chem Mater*. **2007**, 19(18), 4396–4404.
17. X. Lu, M. Yu, H. Huang, R. S. Ruoff, *Nanotechnology*, **1999**, 10(3), 269–272.
18. M. Choucair, P. Thordarson, J. A. Stride, *Nat. Nanotechnol.*, **2009**, 4, 30–33.
19. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon*, **2007**, 45, 1558–1565.

Povzetek

Grafen je poznan po svojih izjemnih lastnostih: je trdnejši od diamanta, bolje prevaja električni tok kot baker in je upogljivejši od gume. Zaradi njegove potencialne uporabe v industriji je vedno več poskusov iskanja novih – manj toksičnih in cenejših – načinov njegove priprave. V tem delu je predstavljena učinkovita metoda priprave grafena z elektrolizo pri visoki temperaturi. Mikrostrukturo produkta smo ovrednotili z vrstično elektronsko mikroskopijo visoke ločljivosti in Ramansko spektroskopijo.

Njegove elektrokemijske lastnosti smo proučevali s ciklično voltometrijo in meritvami AC impedance. Rezultati kažejo, da gre za monoplastno strukturo grafen, ki je optimalna, če poteka elektroliza pri napetosti 1.5 V. Pri gostoti toka 1 mA/cm² lahko specifična kapaciteta superkondenzatorja z grafenom doseže tudi do 78.01 F/g v 6 M KOH.