Supporting information

Grafting conductive polymers on graphene oxide through cross-linker: a stepwise approach

Rizwan Khan[a] and Yuta Nishina[* a,b]

[a] *Graduate school of natural science and technology, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan*
[b] *Research Core for Interdisciplinary Sciences, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan*

E-mail: nisina-y@cc.okayama-u.ac.jp.

1. Structure Analysis

Table S1. Quantitative comparison of detected elements from XPS spectra

Sample	Element (at.%)			
	C	O	N	S
GO 3	81.1	11.0	6.5	1.6
GO 2	76.6	17.5	4.1	1.2
GO 1	71.9	25.6	2.4	--

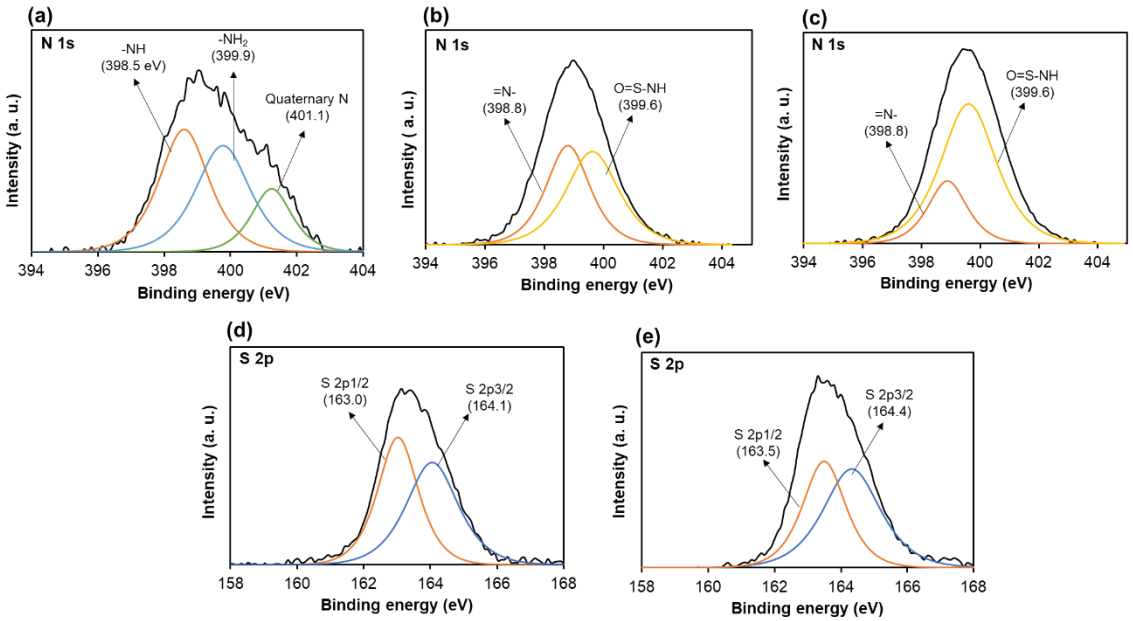
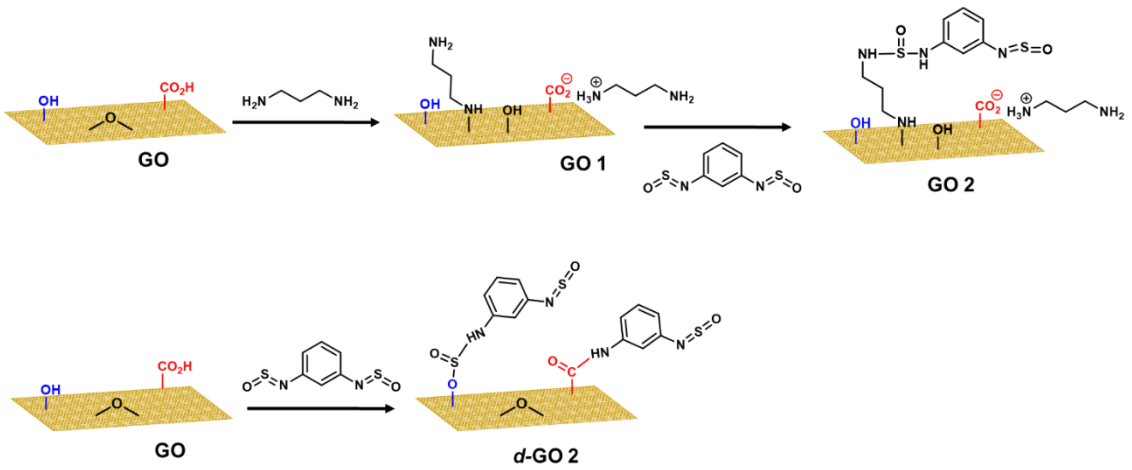


Fig. S1. Narrow scan XPS spectra of (a) N 1s of (a) **GO 1**, **(b) GO 2**, **(c) GO 3** and S 2p of (d) **GO 2**, and (e) **GO 3**

Comparison of GO 2 and *d*-GO 2

The direct reaction of the meta monomer on GO, without 1,3-diaminopropane as a cross-linker, was prepared by the same procedure, except the starting material was GO instead of **GO 1**. The elemental composition of ***d*-GO 2** (without using 1,3-diaminopropane) and **GO 2** (addition of 1,3-diaminopropane) was also measured by XPS analysis, as presented in Fig. S 3. In the case of ***d*-GO 2**, the direct addition of monomer to GO caused the decomposition of the monomer, which might be due to the effect of the carboxylic group of GO [1,2]. In the case of **GO 2**, most of the carboxylic group was neutralized by 1,3-diaminopropane in the first step, which prevented the decomposition of monomer. Therefore, this result confirmed that the addition of 1,3-diaminopropane in the first step is important.



Scheme S1. Synthesis of **GO 2** and ***d*-GO 2**

Table S2. Quantitative comparison of detected elements from XPS spectra

Sample	Element (at.%)			
	C	O	N	S
GO 2	76.6	17.7	4.1	1.2
***d*-GO 2**	76.4	15.5	6.9	1.1

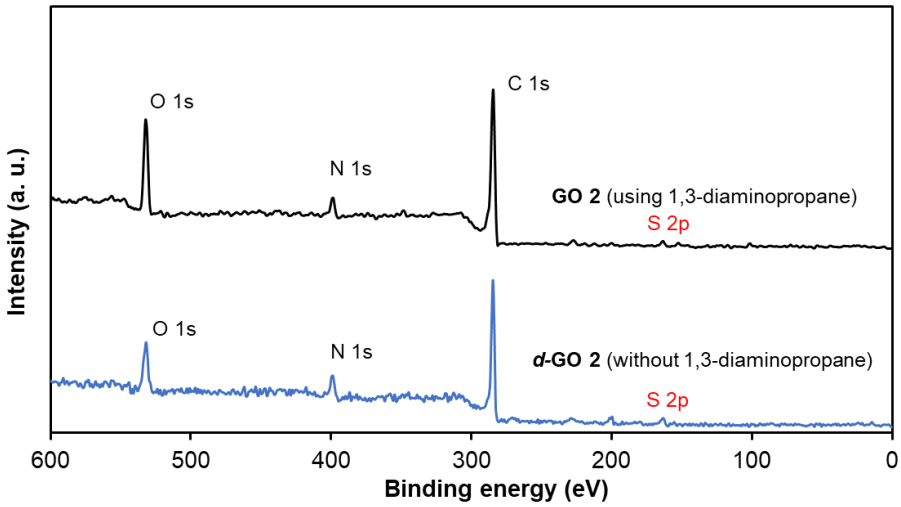
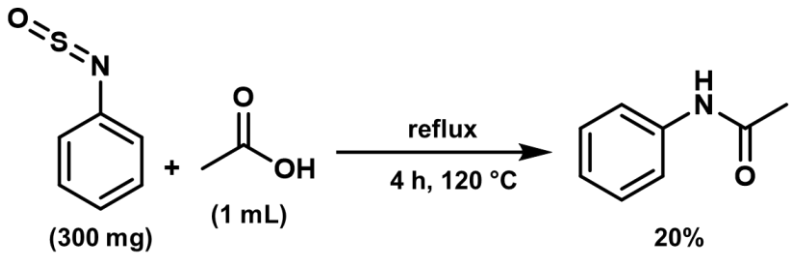


Fig. S2. Wide scan XPS spectra of **GO 2 (**functionalization using 1,3-diaminopropane) and ***d*-GO 2** (functionalization without using 1,3-diaminopropane)



Scheme S2. Possible side reaction between the monomer and carboxylic acid of GO.

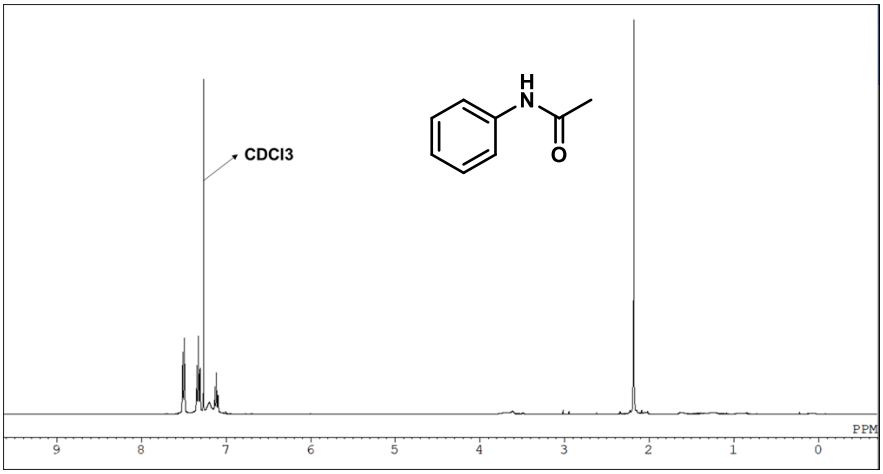


Fig. S3. ^{1}H NMR spectra of the product of Scheme S3.

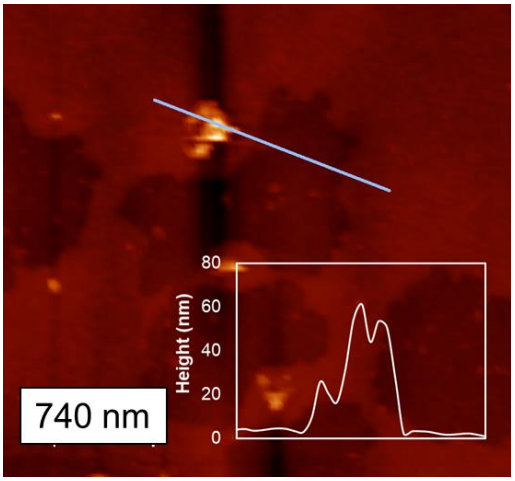


Fig. S4. AFM analysis of just mixing of polymer and graphene

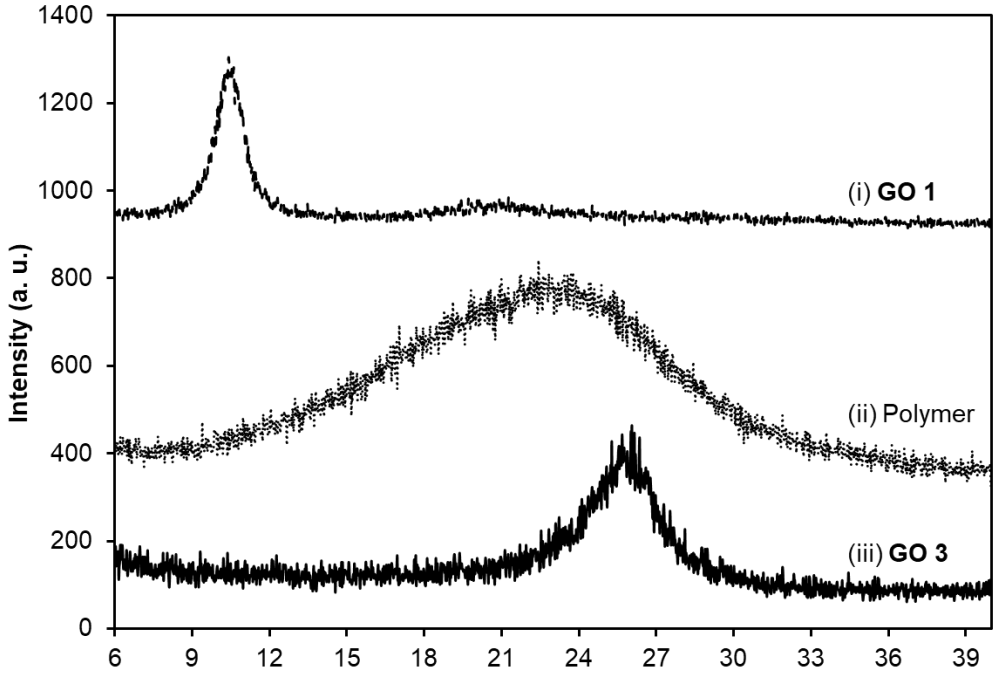


Fig. S5. XRD pattern of (i) **GO 1**, (ii) polymer, and (iii) **GO 3**

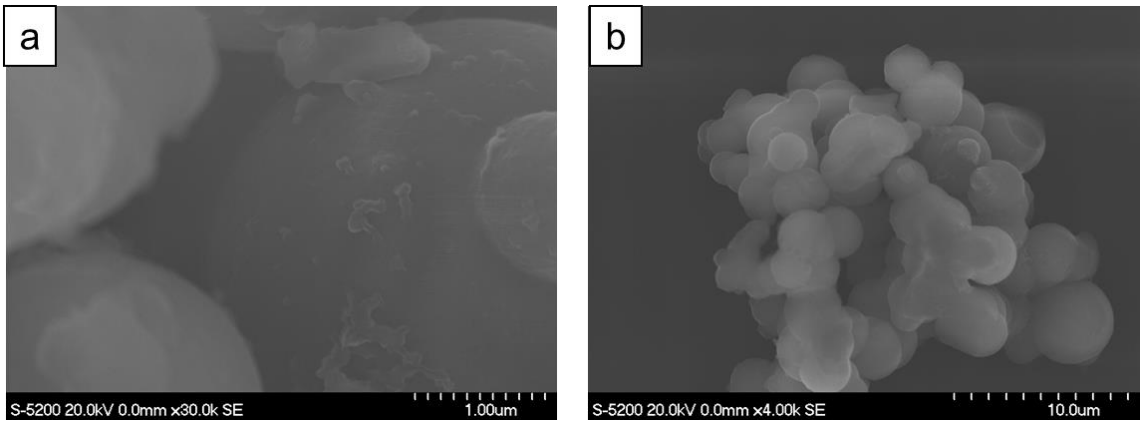


Fig. S6. SEM images of polymer (a) high resolution and (b) low resolution.

2. Electrochemical analysis

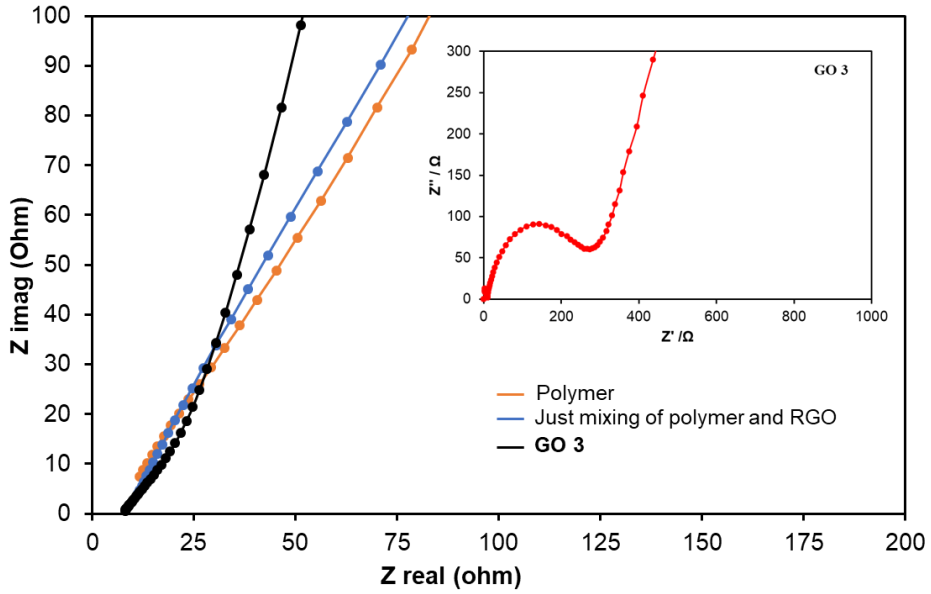


Fig. S7. Nyquist plots of **GO 3**, just mixing of polymer and graphene and only polymer. Inset is the high-frequency plot for **GO 3**.

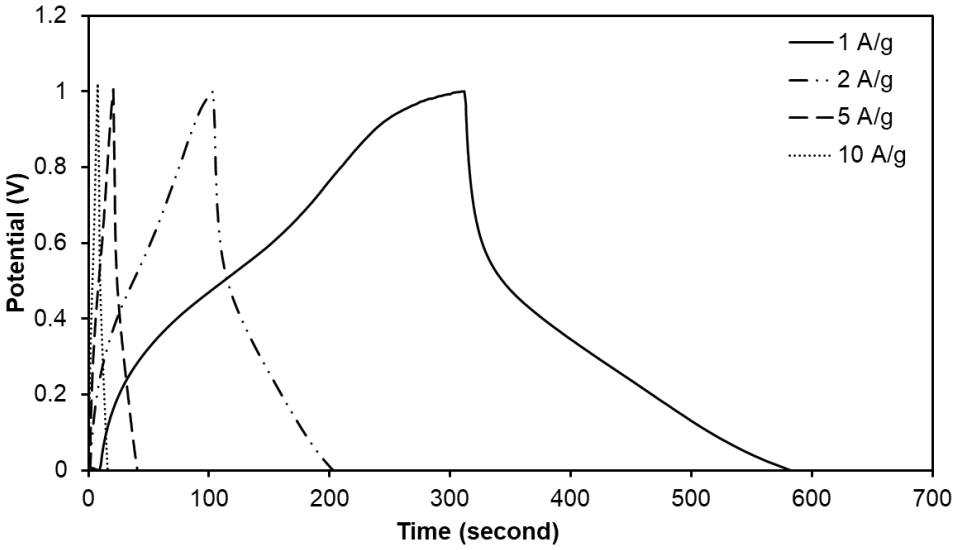


Fig. S8. Galvanostatic charge/discharge curve of **GO 3** at a current density of 1, 2, 5, and 10 A g^{-1}.

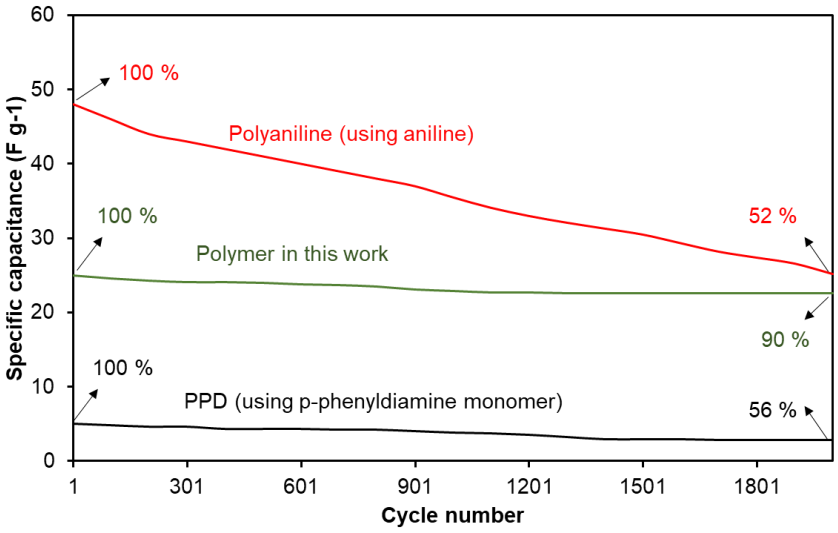


Fig. S9: Cycling stability test of different polymer at a current density of 2 A g^{-1}

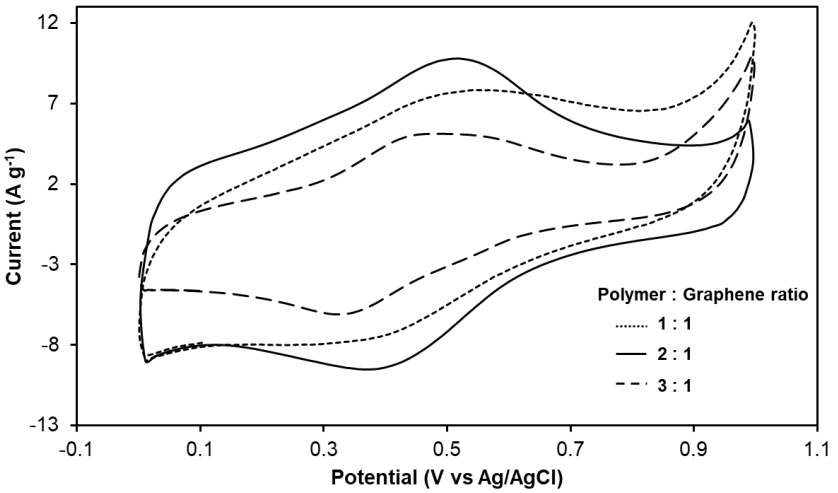


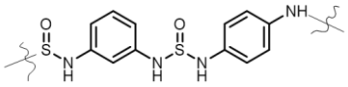
Fig. S10: CV study of **GO 3** with different mass ratios of polymer to graphene at a scan rate of 50 mVs^{-1}.

3. Elemental analysis

Table S3. Quantitative comparison of detected elements from EDS analysis of **GO 3** (different ratios of polymer/graphene).

Polymer:GO (wt ratio)	**Element (at%)**				**Polymer content (wt%)***
	C	O	N	S	
1 : 1	77.7	13.5	6.2	1.2	13.3
2 : 1	80.6	12.0	5.2	1.8	19.9
3 : 1	83.4	10.8	4.3	2.4	26.6

* Polymer contents were calculated based on the molecular weight of the unit and sulfur content. Unit structure for calculation is as follows:



4. Comparison of supercapacitor performance in three-electrode systems

Table S4. Comparison of supercapacitor performance in three-electrode systems.

Material	Cycle number	Capacity retention	Measurement conditions	References
PANI-G	1500	90%	10 A g^{-1}	[3]
PANI-G	1000	91%	2 A g^{-1}	[4]
PANI-G	1500	80%	0.5 A g^{-1}	[5]
PANI-G	200	96%	3 A g^{-1}	[6]
PANI-G	1000	85%	0.5 A g^{-1}	[7]
Ppy-G	1000	92%	1 A g^{-1}	[8]
Ppy-G	200	93%	5 A g^{-1}	[9]
Ppy-G	1500	71%	50 mV s^{-1}	[10]
PEDOT-G	1000	88%	0.3 A g^{-1}	[11]
PEDOT-G	2000	87%	0.5 A g^{-1}	[12]
Ppy-G	500	90%	100 mVs^{-1}	[13]
Ppy-G	1000	91%	1 A g^{-1}	[14]
GO 3	1000	98%	10 A g^{-1}	This work

5. Determination of Capacitive and diffusion controlled contribution

The ratios of capacitive and diffusion were calculated according to the reported method[15] using an equation below.

$i(V) = k_1 v + k_2 v^{1/2}$

$k_1 v$ and $k_2 v^{1/2}$ correspond to the current contributions from the surface capacitive effects and the diffusion-controlled process, respectively.

Table S5. Calculation of Capacitive and diffusion controlled contribution for **GO 3** at 100 mV/sec.

Specific potential	Capacitive charge storage	Diffusion charge storage
0.3 V	71.6 %	29.4 %
0.4 V	62.3 %	37.7 %
0.5 V	64.3 %	35.7 %
0.6 V	82.4%	17.6 %

References

[1] Drageset, V. Elumalai, H. R. Bjersvik, React. Chem.Eng. 3 (2018) 550-558, https://doi.org/10.1039/C8RE00049B

[2] W. T. Smith, G. G. King, J.Org. Chem. 24 (1959) 976-978, https://doi.org/10.1021/jo01089a023

[3] Z. Liu, H. Zhou, Z. Huang, W. Wang, F. Zeng, Y. Kuang, J. Mater. Chem. A. 1 (2013) 3454–3462, https://doi.org/10.1039/C3TA01162C

[4] L. Wang, Y. Ye, X. Lu, Z. Wen, Z. Li, H. Hou, Y. Song, , Sci. Rep. 3 (2013) 3568, 10.1038/srep03568

[5] U. Male, J.K.R. Modigunta, D.S. Huh, Polymer 110 (2017) 242–249, https://doi.org/10.1016/j.polymer.2016.12.031

[6] L. Jianhua, A. Junwei, Z. Yecheng, M. Yuxiao, L. Mengliu, Y. Mei, L. Songmei, ACS Appl. Mater. Inter. 4 (2012) 2870–2876, https://doi.org/10.1021/am300640y

[7] H. Qiu, X. Han, F. Qiu, J. Yang, Appl. Surf. Sci. 376 (2016) 261–268. https://doi.org/10.1016/j.apsusc.2016.03.018

[8] Y. Liu, Y. Zhang, G. Ma, Z. Wang, K. Liu, H. Liu, Electrochim. Acta. 88 (2013) 519–525, 10.1016/j.electacta.2012.10.082

[9] S. Jo, Y.H. Park, S.-G. Ha, S.M. Kim, C. Song, S.Y. Park, I. In, Synthetic Metals. 209 (215) 60–67, https://doi.org/10.1016/j.synthmet.2015.06.004

[10] X. Zuo, Y. Zhang, L. Si, B. Zhou, B. Zhao, L. Zhu, X. Jiang J. Alloys Compd. 688 (2016) 140–148, https://doi.org/10.1016/j.jallcom.2016.07.184

[11] J. Zhang, X.S. Zhao, J. Phys. Chem. C. 116 (2012) 5420–5426, https://doi.org/10.1021/jp211474e

[12] J. Wen, Y. Jiang, Y. Yang, S. Li, J Mater Sci: Mater Electron. 25 (2014) 1063–1071, 10.1007/s10854-013-1687-z

[13] S. Bose, N.H. Kim, T. Kuila, K. Lau, J.H. Lee, Nanotechnology. 22 (2011) 295202, 10.1088/0957-4484/22/29/295202

[14] Y. Song, J.-L. Xu, X.-X. Liu, J. Power Sources, 249 (2014) 48–58, https://doi.org/10.1016/j.jpowsour.2013.10.102

[15] J. Wang, J. Polleux, J. Lim, B. J. Dunn, J. Phys. Chem. C. 111 (2007) 14925-14931, https://doi.org/10.1021/jp074464w