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Graphene/semicrystalline-carbon derived from amylose films for supercapacitor application

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Abstract. Graphene/semicrystalline-carbon in the form of carbon flakes is produced by carbonization up to 600, 700, 800, 900 and 1000°C, respectively, of the amylose films prepared by a casting method on copper foil substrate. The carbon flakes are characterized by X-ray diffraction (XRD) method to determine their microcrystallite interlayer spacing, width and stack-height; and Raman spectroscopy (RS) method to obtain structural information from the D-, D2- and G-bands peak-intensities. The XRD results show that increase in carbonization temperature lead to ~ (1-3 %), ~85 % and ~30 % increase in the microcrystallites interlayer spacing, width and stack-height, respectively, indicating that a larger growth of microcrystallite of carbon flakes occurs in the direction parallel to (001) plane or film planar surface. The specific surface area of carbon flakes estimated from the XRD results in decreases from ~4400 to ~3400 m²/g, corresponding to the specific capacitance between ~500 to ~400 F/g, which are well within the range of specific capacitance for typical electrodes carbon for supercapacitor application. The RS results show that the multilayer graphene co-exist with semicrystalline-carbon within the carbon flakes, with the multilayer graphene relative quantities increase with increasing carbonization temperature.

1. Introduction

Carbon-based materials are known to play a major role in today's science and technology development owing to their wide-spread applications in our everyday life, for example, in devices for energy applications such as supercapacitor, battery and fuel cell [1]. The discovery of graphene may contribute toward widening the areas of these applications. Graphene is made of a single layer of graphite and can be two-dimensional building block for different types of carbon allotropes and it has properties significantly different from graphite composed of many graphitic layers. Graphene can be produced by mechanical cleavage [2,3], chemical vapor deposition [4,5], chemical exfoliation [5,6] and also carbonization method [7-9].

Polymer film can be used as a precursor to produce graphene, for example, by carbonization of nickel-coated polyacrylonitrile polymer [7], SiO₂/Ni coated polystyrene (PS), polyacrylonitrile (PAN),



polymethylmetacrylate (PMMA) [8] and chitosan coated on arbitrary substrates like quartz [9]. In our study, we used a natural polymer namely amylose film coated on copper foil substrate to produce graphene/semicrystalline-carbon by carbonization method. The wheat starch precursor used to prepare amylose film offers advantages over the other polymers mentioned above because of its low cost, ease of film preparation, renewability and abundantly available source. The carbonization temperatures selected for the study were 600 °C to 1000 °C, with increment of 100 °C. The structural changes due to the change in carbonization temperature were investigated by X-ray diffraction (XRD) and Raman spectroscopy (RS) methods. The results obtained from the structural data were used to estimate the specific capacitance of the carbon produced and it was found that the estimated values lie within the range higher than the range typically reported for biomass based carbon electrodes of supercapacitor [10-15].

2. Experimental

The food grade wheat starch powder (7.5 g), glycerol (2.25 ml) and distilled water (150 ml) were mixed together to form a solution which was magnetically stirred for 30 min at 90 °C in water bath. The solution was further stirred for 2 h at room temperature to ensure the complete removal of the bubbles from the prepared viscous solution. This method is commonly used for preparing film from the wheat starch powder [16]. After bubbles removal, 135 ml viscous solution was poured into copper boat (300 mm x 90 mm x 5 mm, constructed using 0.1 mm thick copper foil) and dried in an oven at 50 °C for 24 h to obtain the smooth, homogeneous and wrinkle free film.

After drying, the base of copper boat containing a thin layer of film was cut into four pieces of plates with the size of 25 mm x 250 mm. Eight plates were arranged in stacking and placed in a furnace (Laboratory Tube Furnace VT Furnace CTF – 1100 – 50 – 300) for carbonization [17,18]. The carbonization was conducted in nitrogen environment up to a temperature of 600, 700, 800, 900 and 1000 °C, respectively, to produce graphene/semicrystalline-carbon in the form of flakes. In order to obtain well separated flakes, an aqueous dispersion of 10 mg/ml of carbon flakes was prepared and sonicated for 30 min [19]. Typically 6 g of flakes was poured in 600 ml of distilled water followed by dropwise addition of 10 M aqueous solution of KOH. The solution was sonicated for 3 h at 80 °C in water bath, followed by heating at 50 °C for 24 h [20]. The respective carbon flakes produced were labeled as S600, S700, S800, S900 and S1000.

An X-ray diffractometer (Bruker AXS: model D8 Advance, wavelength of 1.5406 Å for CuK_α line from copper X-ray sources) was used to record the XRD patterns of the S600, S700, S800, S900 and S1000 samples. The Bragg's and Debye-Scherrer equations were used to obtain the structural parameter's values from the XRD spectrum. The Bragg's and Debye-Scherrer's equations are given, respectively, by [21]:

$$n\lambda = 2d \sin \theta; L_{c,a} = \frac{K\lambda}{\beta_{c,a} \cos \theta} \quad (1)$$

where $n = 1$, λ is the wavelength (1.5406 Å) of the X-ray radiation and θ is the Bragg angle representing the position of the (002) and (100) diffraction peaks, from which the interlayer spacing (d_{002} , d_{100}) were determined; and K is the shape factor equal to 0.89 and 1.84 for L_c (stack height of microcrystallite) and L_a (width of microcrystalline) and $\beta_{c,a}$ is the full width at half maximum of the symmetrically shaped (002) and (100) diffraction peaks.

The relationship between L_c and the BET surface area (S) of the carbon material is given by equation [22,23]:

$$S = \frac{2}{\rho_{xrd} L_c} \quad (2)$$

where ρ_{xrd} (X-ray density of carbon) is given by $\rho_{xrd} = (d_{002(\text{graphite})}/d_{002}) \times \rho_{(\text{graphite})}$. The values of $d_{002(\text{graphite})}$ and $\rho_{(\text{graphite})}$ are 0.33354 nm and 0.268 g/cm³, respectively. The surface area (S) is related to the specific capacitance (C_{sp}) of carbon electrodes used in supercapacitor cells by equation [24,25]:

$$C_{sp} = C_{dl} \times \left(\frac{S}{2}\right) \quad (3)$$

where C_{dl} is the electric double layer capacitance. In this study, in order to estimate the C_{sp} values, we assume $S_{BET} \approx S_{xrd}$, and the S_{xrd} values were obtained from the XRD results and the typical C_{dl} value (2.244×10^{-5} F/cm²) was obtained from the literature [26].

Raman spectra for the S600, S700, S800, S900 and S1000 samples were recorded over a Raman shift range from 100 to 3200 cm⁻¹ using a Raman spectrometer (Renishaw in Via Raman microscope) employing a 633 nm laser beam [27].

3. Results and discussion

Figure 1 shows the XRD spectra for the S600, S700, S800, S900 and S1000 samples. All of the carbon samples show similar diffraction patterns with two broad peaks at diffraction angles (2θ) of around 23° and 43°, corresponding to the (002) and (100) diffraction peaks, respectively. This indicates that all samples have a turbostratic structure, which implies that the building blocks of the carbon samples are composed of graphitic-like microcrystallites that are randomly oriented and distributed throughout the samples. From these broad peaks, the values of the structural parameters, such as the interlayer spacing (d_{002} and d_{100}) and microcrystallite dimensions [L_c (stack height) and L_a (width)], were determined using equations (1) mentioned in the experimental section. The calculated values of the structural parameters are shown in table 1. The magnitudes of these parameter values are comparable to those reported for activated carbon supercapacitor electrodes prepared from bulk biomass precursors [10-15]. The d_{002} values are higher than those for the graphite, a common trend found in the literature [27].

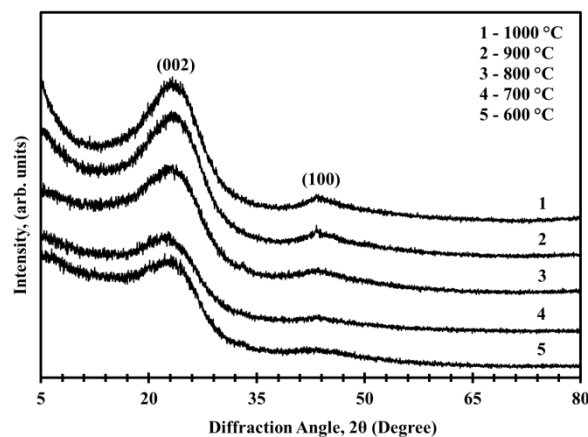


Figure 1. XRD pattern for all carbon flakes.

Table 1. Interlayer spacing, crystallite dimension, and ratios of L_c/L_a and L_c/d_{002} for all carbon flakes.

Samples	d_{002} (Å)	d_{100} (Å)	L_c (Å)	L_a (Å)	L_c/L_a	L_c/d_{002}
S600	3.797	2.073	19.234	28.835	0.667	5.066
S700	3.838	2.078	20.313	32.562	0.624	5.293
S800	3.862	2.087	22.255	37.386	0.595	5.763
S900	3.879	2.092	23.781	45.943	0.518	6.131
S1000	3.904	2.101	25.480	53.287	0.478	6.527

Small increase in the d_{002} (~3 %) and d_{001} (~1 %) values due to the change in the carbonization temperature can also be seen in this table. However, larger increase in L_c (~39 %) and L_a (~85 %) values occurred as the carbonization temperature increases, indicating an effect of increasing temperature on the growth of microcrystallites during carbonization. The ratio of L_c/L_a seems to decrease systematically with increasing carbonization temperature. The trends of these changes indicate that larger change occurs in the (001) plane during carbonization. This is an expected trend because logically it can occur only in the direction that is parallel to film surface where along this direction the atoms are adequately available, in contrast to the (002) direction whose number of atoms are limited by the thickness of the thin film. The data in this table also show that increase in the carbonization temperature does not increase the number of graphitic layer more than two layers in the carbon flakes produced, as revealed by the variation of the ratio L_c/d_{002} values.

The values of specific surface area of carbon flakes estimated using equation (2) are shown in table 2, which are higher than the experimentally recorded specific surface area of activated carbon supercapacitor electrodes prepared from bulk biomass precursors [10-15]. These estimated specific surface area values were used to estimate the specific capacitance (C_{sp}) using equation (3) and the corresponding values were found decrease for S600, S700, S800, S900 and S1000 carbon flakes samples, respectively, as shown in table 2. These values are very much larger than those reported in references [10-15].

Table 2. The surface area and specific capacitance for all carbon flakes.

Samples	S (m ² /g)	C _{sp} (F/g)
S600	4423	496
S700	4226	474
S800	3873	435
S900	3657	410
S1000	3428	385

Figure 2 shows the Raman spectra for all the samples, with the presence of two sharp bands (first order) and a broad band (second order); which are typical bands for carbon materials. The D band at ~1350 cm⁻¹ represents disordered carbon, and G band at ~1580 cm⁻¹ represents ordered carbon. The degree of ordering or disordering in carbon materials can be represented by the ratio of the intensities of the D band and G band (I_D/I_G). Table 3 shows the calculated I_D/I_G values determined from the first order Raman bands in figure 2, which indicate that carbon flakes produced become less ordered with increasing carbonization temperature. The values of the ratio I_D/I_G can be correlated with the values of L_a [27,28]. Our results show that the ratio I_D/I_G is linearly correlated with the values of $1/L_a$ (table 3) as shown in figure 3.

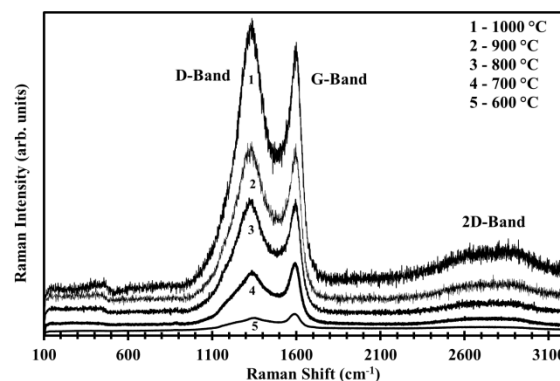
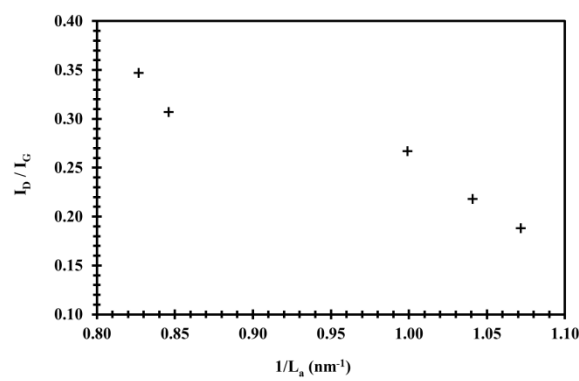


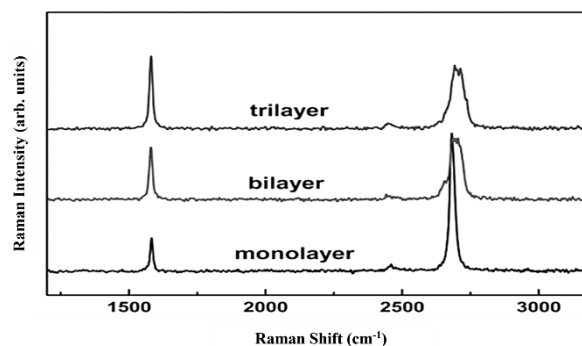
Figure 2. Raman spectra for all carbon flakes.

Table 3. I_D/I_G ratio of D band and G band and $1/L_a$ for all carbon flakes.

Samples	D-Band	G -Band	Ratio D:G	$1/L_a$
S600	21628	26158	0.827	0.347
S700	7529	8899	0.846	0.307
S800	2636	2639	0.999	0.267
S900	1875	1802	1.041	0.218
S1000	2070	1931	1.072	0.188

**Figure 3.** The intensity ratio I_D/I_G for all carbon flakes is plotted versus $1/L_a$.

The broad second order D2-band between 2400 to 3100 cm^{-1} appears to increase in intensity with increasing carbonization temperature. This band behaviour indicates that the multilayers graphene, which co-exist with the semicrystalline carbon in the carbon flakes, increase in quantity with increasing carbonization temperature. It should be noted that similar broad second order bands are observed for the graphene/carbon samples derived from polymer films reported in references [7,8,9]. For a single layer pristine graphene, the 2D-band is very much sharper and typically has higher intensity than that of G-band; and the D-band is not present [29]. Further, as the number of layers increases, the 2D-band becomes more broadened as shown in figure 4 [29].

**Figure 4.** Raman spectra of pristine n-layer graphene [29].

4. Conclusion

GSC has been prepared in the form of carbon flakes by carbonization of amylose film deposited on copper foil substrate over different carbonization temperature (600, 700, 800, 900, and 1000 °C). It has been found that (i) the increase of carbonization temperature causes an increase of ~ (1-3) %, ~85 % and 30 % in micro-crystallites interlayer spacing, width and stacking-height of GSC, respectively, indicating a larger growth of microcrystallites of carbon flakes occurs in the direction parallel to the (001) plane or film planar surface, (ii) the increase of carbonization temperature leads to the decrease in the specific surface area of carbon flakes from ~4400 to ~3400 m²/g, which corresponds to the specific capacitance values ranging from ~500 to ~400 F/g. These values are comparable and even higher than those of many carbon-based electrodes widely used in supercapacitor and (iii) the Raman spectroscopy results demonstrate that the multilayer graphene co-exist with semicrystalline carbon within the carbon flakes produced and the contents of multilayer graphene increase with increasing carbonization temperature.

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References

- [1] Ferrari A C 2007 *Solid State Commun.* **143** 45
- [2] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V, Firsov A A 2004 *Science* **306** 666
- [3] Novoselov K S, Jiang D, Schedin F, Booth T, Khotkevich V V, Morozov S V, Geim A K 2005 *P. Natl. Acad. Sci. USA* **102** 10451
- [4] Oshima C and Nagashima A 1997 *J. Phys. Condens. Matter* **9** 1
- [5] Rosei R, Modesti S and Sette F 1984 *Phys. Rev. B* **29** 3416
- [6] Stankovich S, Dikin D A, Dommett G H B, Kohlhaas K M, Zimmey E J, Stach E A, Piner R D, Nguyen S T and Ruoff R S 2006 *Nature* **442** 282
- [7] Kwon H J, Ha J M, Yoo S H, Ali G and Cho S O 2014 *Nanoscale Res. Lett.* **9** 618
- [8] Byun S J, Lim H, Shin G Y, Han T H, Oh S H, Ahn J H, Choi H C and Lee T W 2011 *J. Phys. Chem. Lett.* **2** 493
- [9] Primo A, Atienzar P, Sanchez E, Delgado J M and Garcia H 2012 *Chem. Commun* **48** 9254
- [10] Farma R, Deraman M, Awitdrus, Talib I A, Taer E, Basri N H, Manjunatha J G, Ishak M M, Dollah B N and Hashmi S A 2013 *Bioresour. Technol.* **132** 254
- [11] Basri N H, Deraman M, Kanwal S, Talib I A, Manjunatha J G, Aziz A A and Farma R 2013 *Biomass Bioenerg.* **59** 370
- [12] Dolah B N M, Deraman M, Othman M A R, Farma R, Taer E, Basri N H, Talib I A, Omar R and Nor N S M 2014 *Mater. Res. Bull.* **60** 10
- [13] Nor N S M, Deraman M, Omar R, Farma R, Basri N H, Dolah B N M, Mamat N F, Yatim B and Daud M N M 2015 *Energy* **79** 183
- [14] Awitdrus, Deraman M, Talib I A, Farma R, Omar R, Ishak M M, Basri N H and Dolah B N M *Adv. Mat. Res.* **501** 13
- [15] Deraman M, Daik R, Soltaninejad S, Nor N S M, Awitdrus, Farma R, Mamat N F, Basri N H and Othman M A R 2015 *Adv. Mat. Res.* **1108**, 1
- [16] He Y, Wang X, Wu D, Gong Q, Qiu H, Liu Y, Wu T, Ma J and Gao J 2013 *Mater. Chem. Phys.* **1**
- [17] Deraman M, Ismail M P and Said M M D 1995 *J. Mater. Sci. Lett.* **14** 781
- [18] Rutledge A R, Venditi R A, Pawlak J J, Patel S and Cibils J L 2008 *BioResources* **3** 1063

- [19] Hernandez Y, Nicolosi V, Lotya M, Blighe F M, Sun Z, De S, McGovern I T, Holland B, Byrne M, Gun'ko Y K, Boland J J, Niraj P, Duesberg G, Krishnamurthy S, Goodhue R, Hutchison J, Scardaci V, Ferrari A C and Coleman J N 2008 *Nat. Nanotechnology* **3** 563
- [20] Li Y, Zijl M V, Chiang S and Pan N 2011 *J. Powers Sources* **196** 6003
- [21] Awitdrus, Deraman M, Talib I A, Omar R, Jumali M H, Taer E and Saman M M 2010 *Sains Malays.* **39** 83
- [22] Dresselhaus M S, Fung A W P, Rao A M, DiVittorio S L, Kuriyama K, Dresselhaus G and Endo M 1992 *Carbon* **30** 1065
- [23] Kumar K, Saxena R K, Kothari R D, Suri K, Kaushik N K and Bohra J N 1997 *Carbon* **35** 1842
- [24] Yoon S, Lee C, Oh S M, Park Y K and Choi W C 2009 *J. Non-Cryst. Solids* **355** 252
- [25] Wiecekand B Twardoc U 2004 *J. Phys. Chem. Solids* **65** 263
- [26] Basri N H, Deraman M, Daik R, Ayob M T, Sahri M I, Nor N S M, Dolah B N M and Soltaninejad S 2015 *Adv. Mat. Res.* **1112** 236
- [27] Roh J S 2008 *Carbon* **9** 127
- [28] Dresselhaus M S, Jorio A, Souza Filho A G, Saito R 2010 *Philos. Trans. R. Soc. A.* **368** 5355
- [29] Chen M, Zhou H, Yu F, Yang H, Wang G, He J and Sun L 2013 *Nanoscale* **5** 8359